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ON A CLASS OF RELATIVISTIC WAVE-EQUATIONS OF SPIN 3/2

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§1. Introduction

It has been shown by the author[1] (1949) that on the basis of the general assumptions which underlie present relativistic quantum mechanics, the most general expression in the Lagrange-function, quadratic in the components of the wave-function ψ, can always be written in the canonical form

$$\psi^\dagger \, \mathrm{D} \, (\alpha^k p_k + \beta\chi) \, \psi, \tag{1 a}$$

where[1] $p_k = -i \, \partial/\partial x^k$, χ is an arbitrary constant of the same dimension as p_k, and D, $\mathrm{D}\alpha^k$, and $\mathrm{D}\beta$ are six hermitian matrices which have the transformation properties given below required to preserve the invariance of expression (1) under all Lorentz transformations. The variation of (1) leads to the wave-equation

$$(\alpha^k p_k + \beta\chi) \, \psi = 0 \tag{1 b}$$

since, the matrix D being non-singular by definition, we can divide by it from the left. It has also been shown (1949, 1951) that for an elementary particle-field the five matrices α^k, β must form an irreducible set and the nucleus of the representation $\mathfrak{R}$, which determines the transformation properties of the wave-function ψ under all Lorentz transformations, must be expressible as a polynominal in them. The representation $\mathfrak{R}$ is determined completely by the six infinitesimal transformations I^{kl} and the matrix **R** representing the improper Lorentz transformation r which reverses the directions of the three space axes.

It is well known that for the three relativistic wave-equations for particles of spin 0, $\frac{1}{2}$ and 1 the I's and the α's are connected by the simplest possible relation between them, namely,

$$\mathrm{I}^{kl} = \alpha^k \alpha^l - \alpha^l \alpha^k, \tag{2}$$

and the I's and α's all satisfy minimal equations of the same degree, namely, 2 for the case of spin $\frac{1}{2}$, and 3 for the cases of spin 0 and 1. On the other

[1] x^0, x^1, x^2, x^3 are the four co-ordinates of a point in space, and the metric tensor is taken as usual in the form $g^{00} = -g^{11} = -g^{22} = -g^{33} = 1$, $g^{kl} = 0$ for $k \neq l$.

hand, it has been shown (Bhabha, 1945) that the imposition of the connection (2) in equations for particles of spin greater than 1 leads to systems in which neither the total charge nor the total energy is always positive. Fierz and Pauli (1939) have given a modification of the original set of equations for particles of spin greater than 1 proposed by Dirac (1936) in which either the total charge or the total energy is positive in every case. In the case of these equations the connection between the I's and α's must therefore be more complicated than (2).[2] These facts suggest the following questions: Firstly, is there some general connection between the minimal equations satisfied by the I's and α's and secondly, are these equations necessarily of the same degree? Thirdly, what are the most general conditions under which either the total energy or the total charge is always positive?

In order to find answers to these questions or to obtain information which may lead to them I have investigated in detail an entire class of wave-equations in which the particle has a maximum spin $\frac{3}{2}$, namely, that class of wave-equations in which the wave-function ψ in (1) transforms according to the representation $\mathscr{R}$ of the full Lorentz group given by

$$\mathscr{R} \sim \mathscr{R}(\tfrac{3}{2}, \tfrac{1}{2}) + \mathscr{R}(\tfrac{1}{2}, \tfrac{1}{2}) \tag{3}$$

This class of equations includes the equation given by Dirac, Fierz and Pauli for a particle of spin $\frac{3}{2}$. It will be shown in this paper that in general there is no necessary connection between the minimal equation of the I's and that of the α's, and indeed whereas in this case the minimal equation of the I's is always of degree 4, the α's can have minimal equations of any integral degree from 2 to 6.

We shall show in passing that there is only one equation in this entire class for which the total charge is always positive, namely the equation equivalent to that of Dirac, Fierz and Pauli for a particle of spin $\frac{3}{2}$. Incidentally, this paper gives the latter equation in the canonical form (1 *b*).

It will also be shown that there is no physically sensible equation in this class for a particle of spin $\frac{3}{2}$ and rest mass zero. Putting $\chi = 0$ in the equation of Dirac, Fierz and Pauli leads to an equation in which the particle has states of spin $\frac{3}{2}$ and of spin $\frac{1}{2}$, in addition to leaving certain solutions undertermined corresponding to the existence of a group of gauge transformations. This statement remains true even when β is singular but not zero.

[2] The connection has been found by K. Gupta (1951) for the equation of the Dirac, Fierz Pauli scheme describing a particle of spin $\frac{3}{2}$, and turns out to be much more complicated than (2). However, in this case, both the I's and α's satisfy minimal equations of the fourth degree.

There is one equation in this class which deserves further investigation. In it the particle has a state of finite rest mass with a spin $\frac{3}{2}$ and a state of zero rest mass with a spin $\frac{1}{2}$. The free charge density is positive definite for the former and exactly zero for the latter.

§ 2. The General Forms of the Matrices D, α^k and β

For any matrix T of the representation $\mathfrak{R}$ representing a Lorentz transformation t with the coefficients t_l^k the matrices D, α^k and β transform according to the following relations which leave the expression (1) invariant.

$$\mathrm{T}^\dagger \mathrm{D}\mathrm{T} = \mathrm{D} \tag{4a}$$

$$\mathrm{T}^{-1} \alpha^k \mathrm{T} = t_l^k \alpha^l \tag{4b}$$

$$\mathrm{T}^{-1} \beta \mathrm{T} = \beta \tag{4c}$$

The components of ψ, and in consequence the matrices of the representation $\mathfrak{R}$ and the matrices D, α^k and β can always be subjected to simultaneous transformations by an arbitrary non-singular matrix s as follows:

$$\psi \to \psi' = s^{-1}\psi \tag{5a}$$

$$\mathrm{D} \to \mathrm{D}' = s^\dagger \mathrm{D} s \tag{5b}$$

$$\alpha^k \to \alpha'^k = s^{-1}\alpha^k s \tag{5c}$$

$$\beta \to \beta' = s^{-1}\beta s \tag{5d}$$

$$\mathrm{T} \to \mathrm{T}' = s^{-1}\mathrm{T}s. \tag{5e}$$

The irreducible representation $\mathfrak{R}(k+l, k-l)$ of the full Lorentz group breaks up if $k \neq l$ into the direct sum of the two irreducible representations $\mathfrak{D}_{k,l}$ and $\mathfrak{D}_{l,k}$ of the proper Lorentz group. The representation $\mathfrak{D}_{k,l}$ gives the transformation properties of a spinor $\phi^{\rho_1\rho_2\ldots\rho_{2k}}_{\dot{a}_1\dot{a}_2\ldots\dot{a}_{2l}}$ having $2k$ undotted and $2l$ dotted indices and symmetric in each set separately. Thus, the components of the wave-function ψ in (1), which transform according to the representation (3), can be arranged in the order

$$\psi = \begin{pmatrix} \phi^{\rho\sigma}_{\cdot\cdot} \\ \phi^{\rho}_{\cdot\dot{\alpha}} \\ \phi^{\alpha} \\ \phi_{\cdot\dot{\alpha}} \end{pmatrix} \tag{6}$$

Moreover, we arrange the six independent components of the first spinor in (6) in a column in the following order $\phi^{11}_{\cdot\dot{1}}, \sqrt{2}\,\phi^{12}_{\cdot\dot{1}}, \phi^{22}_{\cdot\dot{1}}, \phi^{11}_{\cdot\dot{2}}, \sqrt{2}\,\phi^{12}_{\cdot\dot{2}}$,

$\phi^{22}_{\dot{2}}$. Similarly, for the next spinor we take the components in the corresponding order $\phi^{1}_{1\dot{1}}$, $\sqrt{2}\,\phi^{1}_{1\dot{2}}$, $\phi^{1}_{2\dot{2}}$, ..., etc. The third and fourth spinors have only two components each, and we take them in their natural order $\phi^{1}, \phi^{2}, \phi_{\dot{1}}, \phi_{\dot{2}}$.

Now the representations $\mathfrak{D}_{k,l}$ and $\mathfrak{D}_{l,k}$ can be taken in such a form that the improper transformation r which reverses the directions of the three space axes turns an upper undotted index into a lower dotted one and *vice-versa*. With the ordering of the components of ψ just given r must then be represented by the matrix

$$\mathbf{R} = \begin{pmatrix} \cdot & 1_{(6)} & \vdots & \\ 1_{(6)} & \cdot & \vdots & \\ \cdots & \cdots & \cdots & \cdots \\ & & \cdot & 1_{(2)} \\ & & 1_{(2)} & \cdot \end{pmatrix} \tag{7}$$

where a dot or a blank space in a matrix indicates a zero or a block of zeros. $1_{(n)}$ stands for the unit matrix of n rows or columns. The subdivisions of the matrix R into submatrices corresponds to the division of ψ into the four spinors in (6). We have now fixed completely the actual form in which we take the representation $\mathfrak{R}$.

Taking the conjugate complex of a spinor turns a dotted spinor index into an undotted one and *vice-versa*. Thus, $\overline{\phi^{\rho\sigma}_{\cdot\cdot}}$ transforms like a spinor $(\phi)^{\dot{\rho}\dot{\sigma}}_{\dot{\alpha}\dot{\cdot}}$. Hence the most general invariant for all transformations of the proper Lorentz group which is linear in ψ and also in $\bar{\psi}$ is

$$d_1\,\overline{\phi^{\alpha}_{\rho\sigma}}\,\phi^{\rho\sigma}_{\alpha} + d_1'\,\overline{\phi^{\alpha\beta}_{\rho}}\,\phi^{\rho}_{\alpha\beta} + d_2\,\overline{\phi_{\alpha}}\,\phi^{\alpha} + d_2'\,\overline{\phi^{\alpha}}\,\phi_{\alpha}, \tag{8}$$

where d_1, d_1', d_2, d_2' are arbitrary constants. This can be written in the form $\psi^{\dagger}\mathrm{D}\psi$. But the matrix D must also satisfy (4 *a*) with R in place of T. Since $\mathrm{R}^{\dagger} = \mathrm{R}^{-1} = \mathrm{R}$ for the matrix (7), D must commute with R. It follows that $d_1' = d_1$ and $d_2' = d_2$. Hence D must have the form

$$\mathrm{D} = \begin{pmatrix} \cdot & d_1 1_{(6)} & \vdots & \\ d_1 1_{(6)} & \cdot & \vdots & \\ \cdots & \cdots & \cdots & \cdots \\ & & \cdot & d_2 1_{(2)} \\ & & d_2 1_{(2)} & \cdot \end{pmatrix} \tag{9}$$

where d_1 and d_2 must be real numbers since D must be hermitian. Now by a simple transformation of the type (5) we can change the absolute values, but not the signs of d_1, and d_2. Hence, without any loss of generality we may assume

$$d_1 = \pm 1,\ d_2 = \pm 1$$

independently of each other.

The matrix β satisfies the equation (Bhabha, 1949)

$$\beta^2 = \beta. \tag{10}$$

As (4 *c*) shows, β commutes with every matrix T of the representation $\mathscr{R}$. Since $\mathscr{R}(\frac{3}{2}, \frac{1}{2})$ and $\mathscr{R}(\frac{1}{2}, \frac{1}{2})$ are both irreducible and inequivalent, the most general form of β is

$$\beta = \left(\begin{array}{cc|cc} & & & \\ & b_1\, 1_{(12)} & & \\ & & & \\ \hline & & & \\ & & b_2\, 1_{(4)} & \\ & & & \end{array}\right) \tag{11}$$

On account of (10) $b_1 = 0$ or 1 and $b_2 = 0$ or 1 independently of each other. $D\beta$ is then a hermitian matrix, as it must be.

The general structure of the matrices α^j has been given in an earlier paper (Bhabha, 1945). We divide each matrix α^j into submatrices corresponding to the subdivision of ψ as in (6), and label these submatrices $(k', l' \,|\alpha^j|\, k, l)$ according to the suffixes of the corresponding representations $\mathscr{D}_{k,l}$. It has been proved in the paper just mentioned that

$$(k', l' \mid \alpha^j \mid k, l) = 0 \text{ unless } \begin{matrix} k' = k \pm \frac{1}{2} \\ l' = l \pm \frac{1}{2} \end{matrix}. \tag{12}$$

Hence the most general form of α^k is

$$\alpha^k = \begin{pmatrix} \cdot & u^k & v^k & \cdot \\ u'^k & \cdot & \cdot & v'^k \\ w'^k & \cdot & \cdot & z'^k \\ \cdot & w^k & z^k & \cdot \end{pmatrix} \tag{13}$$

Every submatrix in (13) is uniquely determined except for multiplication by an arbitrary numerical factor. It follows from (4 *b*) that R commutes with α^0 and anticommutes with α^1, α^2 and α^3. Using (7) for R it immediately follows that $u'^0 = u^0$, $v'^0 = v^0$, $w'^0 = w^0$ and $z'^0 = z^0$, while $u'^k = -u^k$, $v'^k = -v^k$, $w'^k = -w^k$, and $z'^k = -z^k$ for $k = 1, 2, 3$. Thus,

$$\alpha^0 = \begin{pmatrix} \cdot & u^0 & v^0 & \cdot \\ u^0 & \cdot & \cdot & v^0 \\ w^0 & \cdot & \cdot & z^0 \\ \cdot & w^0 & z^0 & \cdot \end{pmatrix} \tag{14}$$

and

$$\alpha^k = \begin{pmatrix} \cdot & u^k & v^k & \cdot \\ -u^k & \cdot & \cdot & -v^k \\ -w^k & \cdot & \cdot & -z^k \\ \cdot & w^k & z^k & \cdot \end{pmatrix} \text{ for } k = 1, 2, 3 \qquad (15)$$

Further $D\alpha^k$ must be a hermitian matrix. Using the form (9) of D this requires that u^k and z^k should be hermitian matrices, and

$$d_1 v^{k\dagger} = d_2 w^k. \qquad (16)$$

The only arbitrariness that remains in (14) and (15) is that u^k and z^k may each be multiplied by some arbitrary real constant, and v^k by an arbitrary complex one. It can be seen easily that by a simple transformation of the type (5) which does not change either the matrices of the representation $\mathfrak{R}$ or the matrices D and β, v^k can be multiplied by an arbitrarily chosen factor of modulus unity and w^k by its conjugate complex. Thus the arbitrary factor c multiplying v^k can always be taken to be real without loss of generality. The sign of c is immaterial since it can always be reversed by a transformation of the same type.

By a rearrangement of the spinors in (6), in particular by taking them in the order $\phi^{\rho\sigma}_{\alpha}$, ϕ_{α}, $\phi^{\rho}_{\alpha\beta}$, ϕ^{ρ}, which can be done by a transformation of the type (5), we can bring the α^k to the form

$$\alpha^0 = \left(\begin{array}{cc:cc} & & u^0 & v^0 \\ & & w^0 & z^0 \\ \hdashline u^0 & v^0 & & \\ w^0 & z^0 & & \end{array}\right), \quad \alpha^k = \left(\begin{array}{cc:cc} & & u^k & v^k \\ & & w^k & z^k \\ \hdashline -u^k & -v^k & & \\ -w^k & -z^k & & \end{array}\right) \qquad (17)$$

for $k = 1, 2, 3$, which more clearly displays their structure. This transformation brings D and β to the form

$$\mathrm{D} = \left(\begin{array}{cc:cc} & & d_1 1_{(6)} & \cdot \\ & & \cdot & d_2 1_{(2)} \\ \hdashline d_1 1_{(6)} & \cdot & & \\ \cdot & d_2 1_{(2)} & & \end{array}\right), \quad \beta = \left(\begin{array}{cc:cc} b_1 1_{(6)} & \cdot & & \\ \cdot & b_2 1_{(2)} & & \\ \hdashline & & b_1 1_{(6)} & \cdot \\ & & \cdot & b_2 1_{(2)} \end{array}\right) \qquad (18)$$

R now takes the same form as D (with $d_1 = 1$, $d_2 = 1$)

Making a further transformation of the type (5) with a matrix defined by

$$s = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

one at once brings α^k, D and β to the form

$$\alpha^0 = \begin{pmatrix} -\alpha'^0 & \\ & \alpha'^0 \end{pmatrix}, \quad \alpha^k = \begin{pmatrix} & -\alpha'^k \\ \alpha'^k & \end{pmatrix} \tag{19 a}$$

$$\mathrm{D} = \begin{pmatrix} -\mathrm{D}' & \\ & \mathrm{D}' \end{pmatrix}, \quad \beta = \begin{pmatrix} \beta' & \\ & \beta' \end{pmatrix} \tag{19 b}$$

where

$$\alpha'^k = \begin{pmatrix} u^k & v^k \\ w^k & z^k \end{pmatrix}, \quad \mathrm{D}' = \begin{pmatrix} d_1 1_{(6)} & \\ & d_2 1_{(2)} \end{pmatrix}, \quad \beta = \begin{pmatrix} b_1 1_{(6)} & \\ & b_2 1_{(2)} \end{pmatrix} \tag{20}$$

The rest mass of the particle is defined as the value of p^0 for which a non-vanishing solution of (1 *b*) exists with $p^1 = p^2 = p^3 = 0$. When there are several different such solutions the particle is said to have states of different rest mass. The number of independent solutions for the same value of p^0 and their transformation properties under space rotations then determines the spin of the particle in the corresponding mass state. The charge density is given by

$$\psi^\dagger \mathrm{D}\alpha^0 \psi, \tag{21}$$

the current density being zero from symmetry for a particle at rest, while the energy density is given by

$$\psi^\dagger \mathrm{D}\alpha^0 p^0 \psi. \tag{22}$$

Thus to find the values of the rest mass of the particle, and to determine the total charge and energy for them, one has only to deal with the martrices α^0 and β in equation (1 *b*), and the matrix $\mathrm{D}\alpha^0$ in expressions (21) and (22). In consequence of (19), this means that we only have to deal further with the submatrices α'^0, β' and $\mathrm{D}'\alpha'^0$ given by (20).

It has been pointed out already that the submatrices u^k, v^k and z^k are uniquely defined except for multiplication by arbitrary real numbers. To give this fact explicit expression we write instead of (20)

$$\alpha'^k = \begin{pmatrix} a_1 u^k & d_1 c\, v^k \\ d_2 c w^k & a_2\, z^k \end{pmatrix}, \tag{23}$$

where a_1, a_2 and c are arbitrary real numbers and the u^k, v^k and z^k are now fixed matrices. u^k and z^k are hermitian, while it follows from (1 *b*) that

$$w^k = v^{k\dagger} \tag{24}$$

3. The Minimal Equation of the α's

The minimal equations of the α's are all related to each other due to their relativistic covariance properties and it is therefore sufficient to find the minimal equation of any one of them. We therefore bring α^0 to its diagonal form, or in case it is not a diagonalizable matrix, to the nearest canonical form. For this purpose we must now insert in (23) the actual forms of the matrices u^0, v^0 and z^0. They have been given in terms of the Dirac—Fierz—Pauli reduction matrices in my earlier paper ((1945); eqn. (66), (67)). Alternatively, one can proceed by writing down equation (1 *b*) in terms of spinors only, then writing it in the matrix form (1 *b*) and finally take for α^0 the matrix which multiplies p_0 (cf. Gupta, 1951). In this way we find that

$$u^0 = \begin{bmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \frac{1}{2} & \cdot & \frac{1}{\sqrt{2}} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \frac{1}{\sqrt{2}} & \cdot \\ \cdot & \frac{1}{\sqrt{2}} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \frac{1}{\sqrt{2}} & \cdot & \frac{1}{2} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix} \tag{25 a}$$

$$v^0 = \begin{pmatrix} \cdot & \cdot \\ \frac{1}{2} & \cdot \\ \cdot & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \cdot \\ \cdot & -\frac{1}{2} \\ \cdot & \cdot \end{pmatrix} \tag{25 b}$$

while z^0 is simply the unit matrix of degree 2. (24) shows that $w^0 = v^{0\dagger} = \tilde{v}^0$. Hence, substituting these matrices in (23), we get

$$\alpha'^0 = \left[\begin{array}{cccccc|cc} a_1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \frac{1}{2}a_1 & \cdot & \frac{1}{\sqrt{2}}a_1 & \cdot & \cdot & \frac{1}{2}d_1c & \cdot \\ \cdot & \cdot & \cdot & \cdot & \frac{1}{\sqrt{2}}a_1 & \cdot & \cdot & \frac{1}{\sqrt{2}}d_1c \\ \cdot & \frac{1}{\sqrt{2}}a_1 & \cdot & \cdot & \cdot & \cdot & -\frac{1}{\sqrt{2}}d_1c & \cdot \\ \cdot & \cdot & \frac{1}{\sqrt{2}}a_1 & \cdot & \frac{1}{2}a_1 & \cdot & \cdot & -\frac{1}{2}d_1c \\ \cdot & \cdot & \cdot & \cdot & \cdot & a_1 & \cdot & \cdot \\ \hline \cdot & \frac{1}{2}d_2c & \cdot & -\frac{1}{\sqrt{2}}d_2c & \cdot & \cdot & a_2 & \cdot \\ \cdot & \cdot & \frac{1}{\sqrt{2}}d_2c & \cdot & -\frac{1}{2}d_2c & \cdot & \cdot & a_2 \end{array}\right] \tag{26}$$

We first note that in each of the first and sixth rows and columns there is only one element. Secondly, there are non-vanishing elements at the intersections of the second, fourth and seventh rows and columns, but none where any of these crosses any other row or column. Similarly, there are non-vanishing elements at the intersections of the third, fifth and eighth rows and columns, but none where these intersect any of the others. Hence by a simple rearrangement of the rows and columns in (26) and a multiplication of some of these by -1 we can bring α'^0 to the form

$$\alpha'^0 \to \begin{pmatrix} a_1 & & & \\ & a_1 & & \\ & & \alpha'' & \\ & & & \alpha'' \end{pmatrix} \text{ where } \alpha'' = \begin{pmatrix} \frac{1}{2}a_1 & \frac{1}{\sqrt{2}}a_1 & \frac{1}{2}d_1c \\ \frac{1}{\sqrt{2}}a_1 & \cdot & -\frac{1}{\sqrt{2}}d_1c \\ \frac{1}{2}d_2c & -\frac{1}{\sqrt{2}}d_2c & a_2 \end{pmatrix} \tag{27}$$

This rearrangement of the rows and columns is simply a transformation of the type (5) with a suitably chosen s. It produces corresponding transformations in $\mathbf{D}'$ and β' given by (5 *b*) and (5 *d*). Thus $\mathbf{D}'$ is transformed to

$$\mathbf{D}' \to \begin{pmatrix} d_1 & & & \\ & d_1 & & \\ & & \mathbf{D}'' & \\ & & & \mathbf{D}'' \end{pmatrix}, \text{ where } \mathbf{D}'' = \begin{pmatrix} d_1 & \cdot & \cdot \\ \cdot & d_1 & \cdot \\ \cdot & \cdot & d_2 \end{pmatrix} \tag{28}$$

and β' to

$$\beta' \to \begin{pmatrix} b_1 & & & \\ & b_1 & & \\ & & \beta'' & \\ & & & \beta'' \end{pmatrix} \text{ where } \beta'' = \begin{pmatrix} b_1 & \cdot & \cdot \\ \cdot & b_1 & \cdot \\ \cdot & \cdot & b_2 \end{pmatrix} \tag{29}$$

To proceed further we only need to deal with the submatrices α'', D'' and β''. It is quite easy to see by a little calculation that the characteristic equation of α'' has the root a_1, so that a_1 must be an eigen-value of α'' irrespective of the values of a_2, d_1c, and d_2c. Indeed, taking

$$s = \begin{pmatrix} \frac{1}{\sqrt{3}} \begin{pmatrix} \sqrt{2} & 1 \\ 1 & -\sqrt{2} \end{pmatrix} & \cdot \\ \cdot & 1 \end{pmatrix} \tag{30}$$

so that $s^{-1} = s = s^{\mathrm{T}}$, we find that

$$s^{-1}\,\alpha''\,s = \begin{pmatrix} a_1 & \cdot \\ \cdot & \zeta \end{pmatrix} \tag{31 a}$$

where

$$\zeta = \begin{pmatrix} -\frac{1}{2}a_1 & \frac{\sqrt{3}}{2}d_1c \\ \frac{\sqrt{3}}{2}d_2c & a_2 \end{pmatrix} \tag{31 b}$$

$$s^{-1}\,D''s = D'' = \begin{pmatrix} d_1 & \cdot \\ \cdot & \eta \end{pmatrix} \text{ where } \eta = \begin{pmatrix} d_1 & \cdot \\ \cdot & d_2 \end{pmatrix} \tag{32}$$

$$s^{-1}\,\beta''s = \beta'' = \begin{pmatrix} b_1 & \cdot \\ \cdot & \xi \end{pmatrix} \text{ where } \xi = \begin{pmatrix} b_1 & \cdot \\ \cdot & b_2 \end{pmatrix} \tag{33}$$

Thus, inserting (31), (32) and (33) into (27), (28) and (29) respectively, and rearranging the rows and columns we find that

$$\alpha'^0 \to \begin{pmatrix} a_1 1_{(4)} & \cdot & \cdot \\ \cdot & \zeta & \cdot \\ \cdot & \cdot & \zeta \end{pmatrix}, \quad D' \to \begin{pmatrix} d_1 1_{(4)} & \cdot & \cdot \\ \cdot & \eta & \cdot \\ \cdot & \cdot & \eta \end{pmatrix}, \quad \beta' \to \begin{pmatrix} b_1 1_{(4)} & \cdot & \cdot \\ \cdot & \xi & \cdot \\ \cdot & \cdot & \xi \end{pmatrix} \tag{34}$$

The characteristic equation of ζ is

$$|\lambda - \zeta| = \lambda^2 + (\tfrac{1}{2}a_1 - a_2)\lambda - (\tfrac{1}{2}a_1 a_2 + \tfrac{3}{4}d_1d_2c^2) = 0. \tag{35}$$

If λ_1 and λ_2 are the two eigen-values of ζ, then

$$\left.\begin{matrix}\lambda_1 \\ \lambda_2\end{matrix}\right\} = -\tfrac{1}{2}(\tfrac{1}{2}a_1 - a_2) \pm \tfrac{1}{2}\sqrt{(\tfrac{1}{2}a_1 + a_2)^2 + 3d_1d_2c^2}. \tag{36}$$

We have now to distinguish between two possibilities. First, if $\lambda_1 \neq \lambda_2$, then ζ must be a diagonalizable matrix, since each eigen-value can occur only once, and a matrix s must exist such that

$$s^{-1}\,\zeta\, s = \begin{pmatrix} \lambda_1 & \cdot \\ \cdot & \lambda_2 \end{pmatrix} = \zeta' \text{ (say)}. \tag{37}$$

Secondly, if $\lambda_1 = \lambda_2 = \lambda$ say, then ζ cannot be diagonalizable, since otherwise it would simply become a multiple of the unit matrix, and any transformation of the type (37) would require ζ to be likewise a multiple of the unit matrix. In this case, however, a matrix s exists which brings ζ to its pseudo-diagonal form

$$s^{-1}\,\zeta\, s = \begin{pmatrix} \lambda & 1 \\ \cdot & \lambda \end{pmatrix} = \zeta' \text{ (say)}. \tag{38}$$

A simple calculation shows that a matrix s satisfying (37) is given by

$$s = \begin{pmatrix} f & \frac{\sqrt{3}}{2}\, d_1 c \\ \frac{\sqrt{3}}{2}\, d_2 c & -f \end{pmatrix} \frac{1}{\sqrt{f^2 + \frac{3}{4} d_1 d_2 c^2}}. \tag{39}$$

where

$$f \equiv -\tfrac{1}{2}(\tfrac{1}{2}a_1 + a_2) + \tfrac{1}{2}\sqrt{(\tfrac{1}{2}a_1 + a_2)^2 + 3d_1 d_2 a^2} \tag{40}$$
$$= \lambda_1 - a_2 = -(\lambda_2 + \tfrac{1}{2}a_1).$$

The last two relations follow from (36). The matrix (39) satisfies $s^{-1} = s$. The physically significant equations are only those in which λ_1 and λ_2, and therefore f, are real. It is not necessary, even so, that the square root in (39) should be real. It is important to note in connection with the transformation of η that $s^{\dagger}\eta\, s = \pm\, \eta$, the plus or minus sign being taken depending on whether the square root in (39) is real or imaginary. In the case (38)

$$\lambda_1 = \lambda_2 = \lambda\,(\text{say}) = -\tfrac{1}{2}(\tfrac{1}{2}a_1 - a_2) \tag{41 a}$$

or

$$\lambda - a_2 = -(\lambda + \tfrac{1}{2}a_1) = -\tfrac{1}{2}(\tfrac{1}{2}a_1 + a_2) = f, \tag{41 b}$$

and the expression under the square root in (36) must vanish. That is,

$$(\tfrac{1}{2}a_1 + a_2)^2 + 3d_1\, d_2 c^2 = 0 \tag{42}$$

from which follows[3]

$$d_1\, d_2 = -1,\ \sqrt{3}c = -(\tfrac{1}{2}a_1 + a_2) = f. \tag{43}$$

[3] We take the positive sign for c since the sign of c is immaterial, as already pointed out earlier.

Then a matrix s satisfying (38) is given by

$$s = \begin{pmatrix} 1 & -d_2 + \frac{1}{f} \\ d_2 & -1 \end{pmatrix} \sqrt{f} \tag{44}$$

This matrix satisfies $s^2 = d_2$ so that $s^{-1} = d_2 s$. (45)

When $\lambda_1 \neq \lambda_2 \neq a_1$, it follows from (19 *a*), (34) and (37) that the minimal equation of α^0 must be[4]

$$\left((\alpha^0)^2 - a_1^2\right)\left((\alpha^0)^2 - \lambda_1^2\right)\left((\alpha^0)^2 - \lambda_2^2\right) = 0. \tag{46 a}$$

It follows from (35) that if

$$\tfrac{1}{2} a_1 a_2 + \tfrac{3}{4} d_1 d_2 c^2 = 0$$

then one of the eigen-values λ_1 or λ_2 is zero, and the minimal equation of α^0 is of the fifth degree, namely,

$$\left((\alpha^0)^2 - a_1^2\right)\left((\alpha^0)^2 - \lambda^2\right)\alpha^0 = 0. \tag{46 b}$$

Similarly, it can be seen without much difficulty that by a suitable choice of the numbers a_2 and c and by taking $d_1 d_2 = \pm 1$ we can arrange either that one of the eigen-values λ_1, λ_2, is $\pm a_1$, the other being λ not $\pm a_1$ nor zero, or that one of them is $\pm a_1$ the other being zero, or that one of them is a_1 and the other $-a_1$. The minimal equation of α^0 in the three cases is then

$$\left((\alpha^0)^2 - a_1^2\right)\left((\alpha^0)^2 - \lambda^2\right) = 0 \tag{47 a}$$

or
$$\left((\alpha^0)^2 - a_1^2\right)\alpha^0 = 0 \tag{47 b}$$

or
$$\left((\alpha^0)^2 - a_1^2\right) = 0. \tag{47 c}$$

This exhausts all the cases in which λ_1 and λ_2 are different from each other, *i.e.*, the cases corresponding to (37) in which α^0 is a diagonalizable matrix.

When the two eigen-values $\lambda_1 = \lambda_2$ are the same and equal to $\lambda \neq \pm a_1$ the minimal equation of α^0 is

$$\left((\alpha^0)^2 - a_1^2\right)\left((\alpha^0)^2 - \lambda^2\right)^2 \tag{48}$$

If $a_2 = -\frac{3}{2} a_1$, then it follows from (41 *a*) that $\lambda = -a_1$, and the minimal equation of α^0 is

$$\left((\alpha^0)^2 - a_1^2\right)^2 = 0. \tag{49}$$

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[4] As shown in the paper quoted above (Bhabha, 1949), the minimal equation of any one of the α matrices immediately determines not only that of all the others, but likewise the general commutation relations satisfied by them. In this case, this relation has to be

$$\Sigma\, (\alpha^h \alpha^i - g^{hi} a_1^2)\,(\alpha^j \alpha^k - g^{jk} \lambda_1^2)\,(\alpha^l \alpha^m - g^{lm} \lambda_2^2) = 0$$

where Σ denotes a sum over all possible permutations of the indices h, i, j, k, l, m. This relation reduces to (46 *a*) if we put all the indices equal to zero.

Finally, if $a_2 = \frac{1}{2} a_1$, then $\lambda = 0$ and the minimal equation is

$$\left((\alpha^0)^2 - a_1^2\right)(\alpha^0)^2 = 0. \tag{50}$$

This exhausts all possibilities of the type (38) in which α^0 has a repeated root and is non-diagonalizable.

Since the wave function ψ always transforms according to the representation (3), it follows that the infinitesimal transformations I^{kl}, or rather the three transformations I^{ok}, always satisfy the same minimal equation of fourth degree, namely,

$$(I^2 - \tfrac{9}{4})(I^2 - \tfrac{1}{4}) = 0. \tag{51}$$

We have therefore proved that *the α-matrices and I's do not necessarily satisfy minimal equations of the same degree, and that for the same set of I's, sets of α's can be found satisfying different minimal equations of different degrees which may be higher or lower than that of the I's.*

The case (47 *c*) deserves special attention, for a consequence of this equation is that the α-matrices now satisfy the commutation relation[5]

$$\alpha^h \alpha^i + \alpha^i \alpha^h - 2g^{hi}(a_1)^2 = 0. \tag{52}$$

which is just the commutation relation satisfied by the Dirac matrices. It follows from (36) that we meet this case when

$$a_2 = \tfrac{1}{2} a_1, \; d_1 d_2 = 1, \; c = + a_1. \tag{53}$$

As is well known, four algebraic quantities satisfying the relation (52) have only one irreducible representation, namely, the one provided by the four Dirac matrices. On the other hand, equation (1 *b*) with the matrices defined by (19 *a*), (23) and (53) is certainly not equivalent to the Dirac equation since the wave-function ψ transforms according to the representation (3), while the Dirac ψ transforms according to the representation $\mathfrak{R}(\frac{1}{2}, \frac{1}{2})$. This apparent contradiction disappears if we realise that with the substitution (53) the four α-matrices given by (19 *a*) and (23) no longer constitute an irreducible set, but become the direct sum of four sets of Dirac matrices. We have here the example of an equation in which the set of four α's is reducible, while the set of eleven matrices consisting of the four α's, the six I's and R is irreducible. In consequence, the I^{kl} cannot be expressed as polynomials of the α's when (53) holds.

The case corresponding to (50) is also worthy of notice, for then the equation (1 *b*) is equivalent to the equation for a particle of spin $\frac{3}{2}$ given by Dirac, Fierz and Pauli. As has already been pointed out, now

[5] See the footnote to formula (46 *a*).

$$a_2 = \tfrac{1}{2}a_1,\ d_1 d_2 = -1,\ c = \frac{1}{\sqrt{3}}a_1 \tag{54}$$

the last relation following form (42). We shall consider this case further in the next section.

§ 4. The Charge Density

In order that an equation should be capable of physical interpretation in the usual manner, either the total charge or the total energy must always be positive for a free particle. The charge density is given by (21), and is always positive if the hermitian matrix $D\alpha^0$ is positive definite. This condition is however too stringent, and it is not necessary for the usual physical interpretation that the matrix $D\alpha^0$ should be positive definite. *It is sufficient if for every ψ corresponding to a free wave-solution of* (1 *b*) *the expression* (21) *is positive*. Whenever this condition is satisfied, we shall say that *the free charge density is positive definite* (even if the matrix $D\alpha^0$ is not positive definite).

The charge density is of course an invariant for every transformation of the type (5). Correspondingly, the positive definite, non-negative or indefinite character of $D\alpha^0$ is likewise invariant for all such transformations. (19 *a*) and (19 *b*) show that this character of $D\alpha^0$ only depends on the corresponding character of $D'\alpha'^0$. It follows from (34) that $D'\alpha'^0$ is equivalent to a direct sum of $d_1 a_1$ and the matrices $\eta\zeta$. From (31 *b*) and (32),

$$\eta\zeta = \begin{pmatrix} -\frac{1}{2} d_1 a_1 & \frac{\sqrt{3}}{2} c \\ \frac{\sqrt{3}}{2} c & d_2 a_2 \end{pmatrix}, \tag{55}$$

which has the characteristic equation

$$\mu^2 + (\tfrac{1}{2} d_1 a_1 - d_2 a_2)\mu - (\tfrac{1}{2} d_1 a_1 d_2 a_2 + \tfrac{3}{4} c^2). \tag{56}$$

Hence, in order that all the eigen-values of $D'\alpha^{0'}$ should have the same sign or that some should be zero and all the rest should have the same sign, the following conditions must be satisfied:—

$$\text{If } d_1 a_1 > 0, \quad \text{then } d_2 a_2 - \tfrac{1}{2} d_1 a_1 \geqslant 0,\ \tfrac{1}{2} d_1 a_1 d_2 a_2 + \tfrac{3}{4} c^2 \leqslant 0, \tag{57 a}$$

which is impossible.

$$\text{If } d_1 a_1 < 0 \quad \text{, then } d_2 a_2 - \tfrac{1}{2} d_1 a_1 \leqslant 0,\ \tfrac{1}{2} d_1 a_1 d_2 a_2 + \tfrac{3}{4} c^2 < 0 \tag{57 b}$$

which is also impossible.

$$\text{If } d_1 a_1 = 0 \quad \text{, then } \tfrac{1}{2} d_1 a_1 d_2 a_2 + \tfrac{3}{4} c^2 = \tfrac{3}{4} c^2 < 0 \tag{57 c}$$

which is also impossible.[6]

[6] Except for the trivial case $a_1 = c = 0$, when the equation reduces to the Dirac equation.

We have therefore proved that *for the entire class of equations under consideration the hermitian matrix* $D\alpha^0$ *cannot be postitive definite, or even non-negative.*[6] It still remains to be investigated whether for any equations of this class *the free charge density* can nevertheless be positive definite.

To investigate this point it is necessary to calculate the charge density for all the free-wave solutions of (1 *b*). This will be done in the next two sections. It is convenient for this purpose to have before us the forms into which η is transformed by the matrices (39) and (44) respectively through a transformation of the type (5).[7]

The matrix (39) which brings ζ to the diagonal form when $\lambda_1 \neq \lambda_2$ transforms η into

$$\eta' = s^\dagger \eta s = \pm \begin{pmatrix} d_1 & \cdot \\ \cdot & d_2 \end{pmatrix} = \pm \eta \tag{58}$$

depending on whether the root in (39) is real or imaginary. It follows that $\eta\zeta$ and ζ are brought simultaneously to the diagonal form through a transformation of the type (5) by the matrix (39).

The matrix (44) transforms η into

$$\eta' = s^\dagger \eta s = \pm d_1 \begin{pmatrix} \cdot & 1 \\ 1 & 2d_1 + \dfrac{1}{f} \end{pmatrix} \tag{59}$$

depending on whether f is positive or negative respectively. In deriving (59) use has to be made of the first equation of (43), namely, $d_1 d_2 = -1$, $d_1 + d_2 = 0$.

§ 5. Values of the Rest Mass and Spin

By a value of the rest mass we mean a value of $\sqrt{p_k p^k}$ for which a non-vanishing solution of equation (1 *b*) exists. In physics we are only interested in equations for which all such values are real. Since this requires the vector p_k to be time-like (or a zero vector) we can always choose a system in which $p_1 = p_2 = p_3 = 0$. The rest mass is therefore a value of $| p_0 |$ for which a non-vanishing solution of the equation

$$(\alpha^0 p_0 + \beta\chi)\psi = 0 \tag{60}$$

[7] Some of this calculation can be avoided by a use of lemma 1, 2 and 3 given in a subsequent paper (Bhabha, 1951, *Phil. Mag.* in course of publication). It can be proved that if α° is a diagonalisable matrix the free charge density can never be positive definite unless the matrix $D\alpha^\circ$ is non-negative. Since (57) proves that $D\alpha^\circ$ is indefinite, the only non-trivial possibility of obtaining a positive definite charge density is by using a non-diagonalizable $\alpha^\bullet$.

exists. It is convenient to treat the cases in which β is non-singular or singular separately.

β non-singular.—It follows from (10) or (11) that if β is non-singular it must be the unit matrix. It has been shown quite generally (Bhabha, 1949) that in this case the values of the rest mass are determined solely by the eigen-values of the matrix α^0. (19 *a*) shows that α^0 is the direct sum of the matrices $\pm \alpha'^0$ so that for every value of p_0 for which a non-vanishing solution of (60) exists, another such independent solution also exists for the value $-p_0$.

(34) shows that α^0 has the eigen-value $-a_1$ four times so that four independent solutions of (60) exist for which $p_0 = \frac{\chi}{a_1}$, provided $a_1 \neq 0$. A rotation of the three space axes leaves α^0 unchanged, but may transform some of these four solutions into each other. An examination of the effect on ψ given by (6) of the transformation s which brings $\alpha^{0\prime}$ to the form (34) shows that one of the four independent solutions is simply provided by the component ϕ_1^{11}. This transforms under space rotations according to the irreducible representation $\mathfrak{D}_{\frac{3}{2}}$ of the three-dimensional orthogonal group. Since this representation is of degree four, it is clear that the four independent solutions of (60) corresponding to the mass value $\frac{\chi}{a_1}$ must transform into each other according to this representation. Thus, in the state of rest mass $\frac{\chi}{a_1}$, the particle would have a spin $\frac{3}{2}$.

If $a_1 = 0$, then (60) requires the four corresponding components of ψ to be zero, irrespective of the value of p_0. Likewise those corresponding to the eigenvalue $-a_1 = 0$, must be zero. There is now no state of rest mass $\frac{\chi}{a_1}$, and the number of independent solutions of equation (1 *b*) is reduced by eight.

If the matrix ζ in (34) has the eigenvalues $\lambda_1 \neq \lambda_2 \neq 0$, and is therefore diagonalizable, then the equation (60) and correspondingly also equation (1 *b*) has solutions corresponding to the values $\frac{\chi}{\lambda_1}$ and $\frac{\chi}{\lambda_2}$ of the rest mass. Each of these occurs twice since ζ occurs twice in (34). An analysis similar to the one already indicated above shows that the particle would have the spin value $\frac{1}{2}$ for each of these two different values of the rest mass. It has already been found in the last section that the transformation which

brings ζ to its diagonal form also diagonalizes η and the charge-density matrix $\eta\zeta$, and that at least one of the eigen-values of the latter must be of opposite sign to the others. The eigen-value of ζ corresponding to this eigen-value of $\eta\zeta$ must be non-zero since η and ζ are both simultaneously diagonalizable. Hence at least one free-wave solution exists for which the charge density has a sign opposite to that of the others, and it follows that *the free charge density cannot be positive definite.*

If either λ_1 or λ_2 is zero, then the corresponding value of the rest mass does not exist, and the number of independent solutions of (1 *b*) is reduced by four. This does not alter the general conclusion regarding the charge density already made in the previous paragraph.[8]

If the two eigen-values of ζ are the same, then it can only be brought to the form (38). The corresponding part of equation (60) then becomes

$$\left\{-\begin{pmatrix}\lambda & 1\\ . & \lambda\end{pmatrix} p_0 + \begin{pmatrix}1 & .\\ . & 1\end{pmatrix}\chi\right\}\begin{pmatrix}\psi_r\\ \psi_s\end{pmatrix} = 0. \tag{61}$$

There is now only *one* independent solution of (61), instead of two. This is ψ_r arbitrary, $\psi_s = 0$, and requires $p_0 = \frac{\chi}{\lambda}$. Using (59) and (38) it is easy to see that *the charge density for this state is exactly zero.* This shows that when α^0 has a repeated eigen-value we do not meet with negative charge densitities but with the new feature of zero charge density. Such states would require a novel physical interpretation. The free charge density is no longer indefinite, as in the previous case, but it is also *not positive definite.*

When $\lambda = 0$, then the one independent solution mentioned above ceases to exist. Equation (1 *b*) now only has free solutions corresponding to the value $\frac{\chi}{a_1}$ of the rest mass, and the free charge density is then positive definite. This corresponds to the equation of Dirac, Fierz and Pauli. We have incidentally proved that it is the only equation of the class under investigation for which the free charge density is positive definite.

β Singular.—Now β has the general form (18) with either b_1, or b_2 or both zero. It has been proved that β can be transformed to the form given by (19 *b*) and (34) simltaneously with α^0 being brought to the form given by (19 *a*) and (34*j*. Hence corresponding to the eigenvalue $-a_1$ of α^0 we now have as before four independent solutions of (60) with $p_1 = \frac{\chi b_1}{a_1}$.

[8] Except for the trivial case $a_1 = c = 0$ already mentioned.

If $b_1 = 1$, this leads to a particle of mass $\frac{\chi}{a_1}$, and spin $\frac{3}{2}$ as before. If $b_1 = 0$, we have a particle of mass zero and spin $\frac{3}{2}$.

In finding the other solutions of (60) we treat the three cases $b_1 = b_2 = 0$, $b_1 = 1$, $b_2 = 0$ and $b_1 = 0$ $b_2 = 1$ separately. In the first case we diagonalize ζ as before. If *neither* of the eigenvalues of ζ are zero, then we have solutions only for $p_0 = 0$ corresponding to two independent states of the particle, each of spin $\frac{1}{2}$, as before. The difficulties regarding the charge density are the same as before. If either (or both) of the eigen-values of ζ is zero, then equation (60) and therefore (1 *b*) has solutions for arbitrary values of p_0. Equation (1 *b*) therefore ceases to define some of the components of ψ completely. This arbitrariness usually corresponds to the existence of a group of gauge transformations, like the well-known gauge transformations for the potentials in the case of the Maxwell equations. But in this particular case some of the arbitrary solutions make a contribution to the charge density.

When either $b_1 = 1$ and $b_2 = 0$, or $b_1 = 0$ and $b_2 = 1$, it is no longer convenient to diagonalize the matrix ζ since this may transform ξ given by (33) into a non-diagonal matrix. It is therefore more convenient to solve directly the corresponding part of equation (60), namely, the equation obtained by writing $-\zeta$ for α^0 and ξ for β.

$$\left\{ -\begin{pmatrix} -\frac{1}{2}a_1 & \frac{\sqrt{3}}{2}d_1 c \\ \frac{\sqrt{3}}{2}d_2 c & a_2 \end{pmatrix} p_0 + \begin{pmatrix} b_1 & \cdot \\ \cdot & b_2 \end{pmatrix} \chi \right\} \begin{pmatrix} \psi_r \\ \psi_s \end{pmatrix} = 0 \qquad (62)$$

If $b_1 = 1$, $b_2 = 0$, then (62) has non-vanishing solutions only if

$$p_0 = 0 \qquad (63\,a)$$

or

$$p_0 = -\frac{2a_2\chi}{a_1 a_2 + \frac{3}{2}d_1 d_2 c^2} \qquad (63\,b)$$

provided the denominator of (63 *b*) does not vanish. In the former case the solution is

$$\psi_r = 0,\ \psi_s \text{ arbitrary}, \qquad (64\,a)$$

in the latter it is

$$\psi_r = -\frac{2d_2 a_2}{\sqrt{3}\,c}\psi_s,\ \psi_s \text{ arbitrary}. \qquad (64\,b)$$

Remembering (55) and using (64) the corresponding charge density turns out to be

$$d_2 a_2 \psi_s \psi_s \qquad (65\,a)$$

in the former, and

$$-\left(\tfrac{3}{8}\, d_1 a_1 \frac{a_2^2}{c^2} + d_2 a_2\right) \bar{\psi}_s \psi_s \tag{65 b}$$

in the latter case. The free charge density is again not positive definite. The particle has states of rest mass $\frac{\chi}{a_1}$, 0 and (63 *b*). If further $a_1 = 0$, then the states corresponding to the first mass value disappear.

On the other hand, if $a_1 \neq 0$, but $a_2 = 0$, then (62) has a non-vanishing solution for only one value of p_0, namely, $p_0 = 0$, as follows from (63 *b*). There is then only one independent solution, namely (64 *a*) with the charge density (65 *a*), that is zero. This is consistent with the physical requirements for a particle of rest mass zero, for such a particle would always travel with the velocity of light and create an infinite field if it had a charge. It is interesting to note that in this equation the particle has two mass states of which one is zero and one finite, namely $\frac{\chi}{a_1}$. This equation deserves further investigation which will be reserved for another occasion.

If the denominator of (63 *b*) vanishes, then again (62) only has non-vanishing solutions for $p_0 = 0$, and indeed, there is then only one independent solution, namely (64 *a*) with the charge density (65 *a*). However, the vanishing of the denominator of (63 *b*) requires that $d_1\, a_1\, d_2\, a_2$ should be negative, that is, that $d_2\, a_2$ should have the oppositite sign to $d_1\, a_1$. It therefore follows from (65 *a*) that for the state of zero rest mass the charge density must be negative, making the equation unsuitable for physical application.

If $b_1 = 0$, $b_2 = 1$, (62) has non-vanishing solution only if

$$p_0 = 0 \tag{66 a}$$

or

$$p_0 = \frac{a_1 \chi}{a_1 a_2 + \frac{3}{2} d_1 d_2 c^2} \tag{66 b}$$

provided the denominator of (66 *b*) does not vanish, with the solutions

$$\psi_r \text{ arbitrary}, \quad \psi_s = 0 \tag{67 a}$$

and

$$\psi_r \text{ arbitrary}, \quad \psi_s = \frac{d_1 a_1}{\sqrt{3}\, c}\, \psi_r. \tag{67 b}$$

The corresponding values of the charge densities are

$$-\tfrac{1}{2}\, d_1 a_1\, \bar{\psi}_r \psi_r \tag{68 a}$$

and

$$\left(\tfrac{1}{2} d_1 a_1 + d_2 a_2 \frac{a_1^2}{3c^2}\right) \bar{\psi}_r\, \psi_r. \tag{68 b}$$

The particle would now have only two values of the rest mass, namely 0 and (66 *b*). The free charge density is however not positive definite, as (68 *a*) shows. We cannot further put $a_1 = 0$ in this case, since then the first four components, corresponding to the eigenvalue $-a_1$ of a^0 can be non-zero even for arbitrary values of p_0.

If the denominator of (66 *b*) vanishes, then non-vanishing solutions exist only for $p_0 = 0$, and indeed, there is then only one independent solution, namely, (67 *a*). However, the charge density for this solution, as given by (68 *a*) is always opposite to that of the principal solution.

Summary

The entire class of relativistic wave equations derivable from the Lagrange function $\psi^\dagger D (a^k p_k + \beta\chi) \psi$ and in which the wave function transforms according to the representation $\mathcal{R}(\frac{3}{2}, \frac{1}{2}) + \mathcal{R}(\frac{1}{2}, \frac{1}{2})$ of the Lorentz group is studied. It is shown that there is only one equation in this class describing particles of finite mass in which the charge density is positive definite, namely, the equation equivalent to the set proposed by Dirac, Fierz and Pauli for a particle of spin $\frac{3}{2}$.

It is shown that there is no equation in this class which describes a particle of spin $\frac{3}{2}$ and zero rest mass.

There is an equation in this class in which the particle has a state of finite rest mass and spin $\frac{3}{2}$ and another state of zero mass and spin $\frac{1}{2}$. In the former state the free charge density is positive definite in the latter zero.

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ANTHRAQUINONE AND ANTHRONE SERIES

Part IX. Chromatographic Adsorption of Aminoanthraquinones on Alumina

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Correlations between chemical constitution and chromatographic behaviour can only be attempted in molecules of the same or similar types and under specified conditions of chromatographic treatment, since complex solvent-adsorbent, solute-solvent and solute-adsorbent relationships are involved. Changes in the sequence of adsorption of the constituents in a mixture have been observed, both when the adsorbent is changed and when the developing solvent is changed. Thus Strain was able to separate some ternary mixtures in four of the six possible sequences by changing the solvent[1]; and LeRosen found that cryptoxanthin is above lycopene on alumina and on calcium carbonate columns, but the order is inverted on a column of calcium hydroxide, using benzene as developer with all the three adsorbents.[2] An inversion of the sequence of adsorption of *N*-ethyl-*N*, *N'*-diphenylurea and 4-nitro-*N*-ethylaniline was observed by Schroeder when a slight alteration in the composition of the developer (2 or 5% of ethyl acetate in light petroleum) was made.[3]

LeRosen has defined the adsorption affinity R as the rate of movement of the adsorptive zone (mm./min.) divided by the rate of flow of developing solvent.[2] R values have been used for standardizing adsorbents and for determining the efficiency of developers; using the same adsorbent and solvent, R values provide a quantitative measure of the adsorption affinities of a series of compounds which can then be correlated with their chemical constitution.

Hydrogen bonding plays an important part in determining the behaviour of chromatographic systems. Hydrogen bonding between solute and adsorbent increases the strength of adsorption; hydrogen bonding between solute and solvent increases solubility and decreases adsorption of the solute, alcohol and other hydrogen bonding solvents therefore being good eluents. Intramolecular hydrogen bonding or chelation increases solubility in non-polar solvents and tends to decrease adsorption when the adsorptive force

is hydrogen bonding between solute and adsorbent. LeRosen, *et al.*[4] have recently attempted to construct a mathematical function relating the interactions in the chromatographic system to the movement of the adsorptive zone. The adsorption was accounted for in terms of donor-acceptor and hydrogen bonding interactions; the carbon side chain decreased adsorption. Donor values were assigned to O and N, and hydrogen bonding values to OH and NH. The solvents were assigned arbitrary values as competitive agents, and the adsorbent strengths were experimentally evaluated. Rates of movement of chromatographic zones calculated on the basis of assigned values agreed reasonably well with experimental values.

The adsorption of a series of nitro compounds on a column of silica gel mixed with Celite 535 has been studied by Schroeder[3] and by Ovenston[5] in connection with the analysis of explosives; alumina is valueless for the purpose. Schroeder observed that on silicic acid inversions in the sequence of adsorption by change of developer occurred very frequently; several compounds exhibited the undesirable effect of "double zoning"—the production of two zones when each of two zones of a mixture separated chromatographically is eluted and re-chromatographed. Using benzene-ligroin or ether-ligroin for development, Schroeder made the following generalizations about the effect of the number and position of substituent groups on the relative adsorption affinity of diphenylamine and its derivatives. Diphenylamine was very weakly adsorbed, 2-nitrodiphenylamine slightly more strongly, and 4-nitrodiphenylamine much more strongly. Chelation of the 2-nitro with the imino group was regarded as being responsible for the low adsorption affinity of the 2-nitro compound, an effect so marked that the 2:2′:4-trinitro and 2:2′:4:4′-tetranitro derivatives were less strongly adsorbed than 4:4′-dinitrodiphenylamine.[6] An *N*-nitroso group was able either to increase or decrease adsorption affinity, as shown by the following increasing order of adsorbability: diphenylamine, *N*-nitrosodiphenylamine, *N*-nitroso-4-nitrodiphenylamine, 4-nitrodiphenylamine. The influence of intramolecular hydrogen bonding, and of hydrogen bonding between the adsorbed compound and the adsorbent (silicic acid), on the adsorption affinities of derivatives of diphenylamine and *N*-ethylaniline has been studied by Schroeder.[6]

Examining the chromatographic separation of a series of hydroxyanthraquinones on silica gel, Hoyer found that anthraquinones containing hydroxyl groups in the α-positions, because of chelation with the CO groups, percolated readily through the column. The position of the hydroxyl groups was more important than the number, as shown by the fact that 2-hydroxy-

anthraquinone remained adsorbed on the column, while 1:4:5:8-tetrahydroxyanthraquinone passed through.[7]

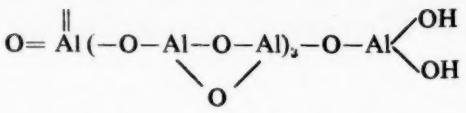
Cropper[8] passed a solution of a mixture of 1- and 2-aminoanthraquinone in toluene-pyridine through alumina and observed that the 1-isomer washes through completely, while the 2- is retained; he noticed two violet zones at the top of the column when technical 1-aminoanthraquinone was chromatographed on alumina from toluene-pyridine solution, and he suggested that these are probably due to the presence of 1:2- and 1:4-diaminoanthraquinones. We have found that technical 1-aminoanthraquinone (I.C.I.) contains at least ten impurities, of which five have so far been identified; these are 2-aminoanthraquinone, and 1:2-, 1:4-, 1:5-, and 1:8-diaminoanthraquinones. Stewart[9] has examined the relation between constitution and chromatographic behaviour of simple anthraquinone derivatives. Subject to the qualification that a change in the activity of the adsorbent by water addition altered the order of movement of the bands, the order of increasing adsorption for monosubstitution was halogen, arylamino, alkylamino, amino, acylamido, side-chain hydroxyl, and nuclear hydroxyl group. It will be clear from the results reported below that the order of separation of acylamidoanthraquinones depends on the position of the substituent and on the presence or absence of an N-alkyl group. Adsorption generally increased with increase in the number of substituent groups, and adsorption from aqueous solution decreased with increase in the number of sulphonic groups. There was no systematic relation between mono-substitution in the 1- and 2-positions.

Discussion of Results

When anthracene, anthraquinone and a series of aminoanthraquinones are chromatographed on alumina, using benzene as solvent for adsorption and development, the strength of adsorption increases in the order shown in Table I.

The aminoanthraquinones (*e.g.*, 1- and 2-aminoanthraquinones, 1:4- and 1:8-diaminoanthraquinones) are useful for standardisation of alumina because they are available commercially, they are easy to purify by crystallization and chromatography, and mixtures separate in distinctly coloured zones.

Alumina active as an adsorbent is prepared by partial dehydration of aluminium hydroxide; the sample used in the present work contained 5·76 per cent. of water. Alekseevskii[10] assigns the structure



to alumina which has been heated to 400° for activation. If the structural units of adsorbent alumina are assumed to be O= Al—O— and O= Al—OH, its affinity for organic molecules will be dependent on the electron-donor character of the oxygen atoms, the hydrogen-bonding ability of the OH group, and the electron-accepting (or Lewis acid) character of aluminium. Interaction between these reactive centres in alumina and corresponding centres in the adsorptive will largely determine the adsorption affinity. From the data obtained for a series of anthraquinone derivatives qualitative correlations of the adsorption affinity with the nature, number and position of substituent groups have been observed. They indicate that, of the various types of interaction of which alumina appears to be capable in the process

TABLE I

Relative adsorption affinities of aminoanthraquinones

Anthracene	Most weakly adsorbed
Anthraquinone	
N-Methyl-1-aminoanthraquinone	
1-Benzamidoanthraquinone	
1 : 4-Bis-methylaminoanthraquinone	
1-Aminoanthraquinone	
1 : 5-Diaminoanthraquinone *	
N-Methyl-2-aminoanthraquinone *	
1 : 8-Diaminoanthraquinone	
N-Methyl-1-benzamidoanthraquinone *	
N-Methyl-2-benzamidoanthraquinone *	
2-Benzamidoanthraquinone	
2-Aminoanthraquinone	
1 : 4-Diaminoanthraquinone	
1 : 4 : 5-Triaminoanthraquinone	
1 : 2-Diaminoanthraquinone	
1 : 4 : 5 : 8-Tetraminoanthraquinone	
2 : 6-Diaminoanthraquinone	Most strongly adsorbed

* These substances do not clearly separate from each other.

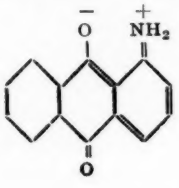
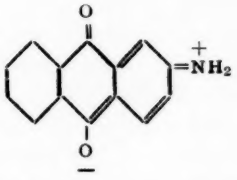
of adsorption, apart from dispersion forces between the adsorbent and adsorptive, the most important is hydrogen bonding between alumina and one or more proton-donor groups in the adsorptive. Although alumina is

a polar adsorbent, the dipole moment or polarizability of the adsorptive plays a less vital role than the availability and accessibility of groups having a hydrogen atom which can take part in the formation of a hydrogen bond. Thus the number and position of the hydroxyl and amino groups profoundly influence the adsorption affinity of an anthraquinone derivative. A complication to be borne in mind in dealing with the hydroxyanthraquinones is the possibility of salt formation and of the formation of co-ordination complexes with alumina. It has been suggested that the stronger adsorption of picric acid in comparison with *o*-nitrophenol, although the latter has a larger dipole moment, is due to the large number of "isolated dipoles" in picric acid[11]; the acid strength of picric acid indicates that salt formation offers a simple explanation.

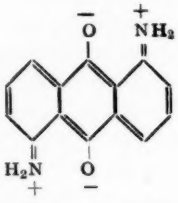
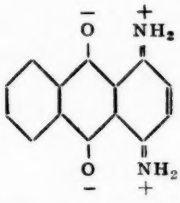
Number of amino groups.—An increase in the number of "anchoring groups", as Zechmeister and others have shown, generally leads to stronger adsorption; this is found to be true of the aminoanthraquinones, if the α- and β-substituted compounds are compared among themselves. Thus relative adsorbability in the α-series is in the increasing order: 1-aminoanthraquinone, the diaminoanthraquinones, 1:4:5-triaminoanthraquinone, and 1:4:5:8-tetraminoanthraquinone; the depth of colour increases in the same order. 2:6-Diaminoanthraquinone is more strongly adsorbed than 2-aminoanthraquinone.

Position of amino groups.—As Hoyer found with the hydroxyanthraquinones, the position of the amino groups is important, but there is a difference between the two substituents in that the α- or β-position is not the over-riding factor when two amino groups are in the 1:4-positions or when the number of amino groups is increased beyond two. The proton-donor properties of the NH_2 group are known to be less than those of the OH group, and infra-red spectra indicate that powerful hydrogen bonding as between the OH and CO groups in the hydroxyanthraquinones does not exist between the NH_2 and CO groups in the aminoanthraquinones, but weak hydrogen bonding is not ruled out.[12] Apparently, the chelation of the α-amino group is strong enough to make the β-amino group more readily available for hydrogen bonding with alumina, resulting in the greater strength of adsorption of β-aminoanthraquinone; we have found that the R_M value[3] of 1-aminoanthraquinone is about nine times that of 2-aminoanthraquinone. 2-Aminoanthraquinone is more strongly adsorbed than 1:5- and 1:8-diaminoanthraquinones, but less strongly adsorbed than 1:4-diaminoanthraquinone. Chelation in the α-aminoanthraquinones is so weak that in 1:4-diaminoanthraquinone (and to an increased extent in 1:4:5-triamino-

and 1 : 4 : 5 : 8-tetraminoanthraquinone) the availability of the amino groups for hydrogen bonding with alumina is sufficient to render them more strongly adsorbed than 2-aminoanthraquinone, but insufficient for increasing the strength of adsorption above that of 2 : 6-diaminoanthraquinone. The greater strength of adsorption of 1 : 8-diaminoanthraquinone in comparison with the 1 : 5-isomer is understandable in view of the independent chelation of each NH_2 with a CO group in the latter compound. Another approach to the relative adsorbabilities of 1- and 2-aminoanthraquinones is to consider the resonance interaction between the NH_2 and one of the CO groups; in the resonance structures (I) and (II) the α-compound will have a considerably smaller dipole moment than the β-, and the strength of adsorption

(I)   (II)

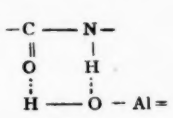
will be correspondingly smaller. Several reasons may be tentatively suggested for the stronger adsorption of 1 : 4-diaminoanthraquinone in comparison with the 1 : 5- and 1 : 8-compounds as well as β-aminoanthraquinone. The influence of the polarization shown in (I) will be to increase the proton-donor character of the NH_2 group in the 4-position. The symmetrical distribution of polarities in 1 : 4-diaminoanthraquinone probably favours adsorption. A comparison of the quadrupolar structures (III) and (IV) for 1 : 5- and 1 : 4-diaminoanthraquinones shows that in (IV) the indicated

(III)   (IV)

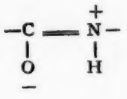
structure will be of relatively low energy and will be stabilized by the naphthalenoid resonance of two rings; it will therefore make a large contribution to the resonance of the molecule. The fact that 1 : 4-diaminoanthraquinone is more deeply coloured than the 1 : 5-isomer can thus be explained. 1 : 4-Diaminoanthraquinone may be expected to have a much larger dipole moment than 1 : 5- or 1 : 8-diaminoanthraquinone.

Acylamido groups.—The effect of *N*-benzoylation is to decrease the strength of adsorption of both 1- and 2-aminoanthraquinones, but for two somewhat different reasons. In α-aminoanthraquinone N-acylation increases the strength of the chelation between the 9-CO and NH groups; and in β-aminoanthraquinone it decreases the resonance interaction between the 10-CO and NH groups. While N-acylation decreases the adsorbability of both 1- and 2-aminoanthraquinone a contrary effect has been noted with other amines. We have observed that the N-benzoyl derivatives of α- and β-naphthylamine in benzene are more strongly adsorbed by alumina than the parent amines. Brockmann found that N-acylation of 4-aminoazobenzene increased the adsorbability on alumina, but 4-aminostilbene and its N-acetyl derivative could not be completely separated; however, the results are not strictly comparable, since benzene was used as the solvent for the azobenzene derivatives and carbon tetrachloride for the stilbene derivatives.[13]

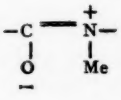
Both amino and amide groups favour adsorption, and the difference in the strength of adsorption due to these two groups appears to be so small that either an amine or its *N*-acyl derivative may be more strongly adsorbed, depending on the nature of the alkyl or aryl residue to which the nitrogen atom in the parent amine is attached and on the nature of the hydrocarbon residue attached to the carbonyl group. The affinity of amides and anilides for water, with which they tend to form complex aggregates, and the association of amides by hydrogen bonding are known.[14] Amide molecules have been found to associate in dilute benzene solutions, the extent of association depending on the nature of the hydrocarbon fraction of the molecule.[15] While amino groups form hydrogen bonds with the oxygen atoms in alumina, amide groups probably interact with the hydroxyl groups in alumina to form complexes of the type (V).



(V)



(VI)



(VII)

The adsorbability of an amide will probably be increased by an increase in the contribution made by the polar resonance structure (VI).[16]

The *N*-benzoyl derivatives of 1- and 2-methylaminoanthraquinone are adsorbed more strongly than the corresponding secondary amines. This is explicable by the increased contribution of the polar resonance structure (VII), in comparison with that of the corresponding structure (VI) for the

molecule not carrying an N-methyl group, as a result of the hyperconjugation effect of the methyl group. The ultraviolet absorption of N-methylacetamide has shown that the molecule resonates between the structures

$$CH_3C{=}ONHCH_3 \longleftrightarrow CH_3\bar{O}C{=}\overset{+}{N}HCH_3,$$

the resonance energy amounting to 16 k cal./mole; because of this resonance *cis-trans* isomerism becomes possible and the *N*-methylacetamide molecule takes the *trans* form.[17]

N-*Alkylation*.—1-Methylaminoanthraquinone, 2-methylaminoanthraquinone and 1 : 4-bis-methylaminoanthraquinone are less strongly adsorbed than the corresponding primary amines. The electron-repulsive effect of the methyl group will be to decrease the proton-donor ability of the amino group in hydrogen bonding, and therefore to decrease the strength of adsorption. Schroeder has observed that 4-nitro-N-ethylaniline is less strongly adsorbed than 4-nitroaniline.[6]

Relative adsorbabilities of aminoanthraquinones and hydroxyanthraquinones.—Phenols in general are more strongly adsorbed than the corresponding primary amines because of the stronger proton-donor character of the hydroxyl group in hydrogen bonding; 2-hydroxyanthraquinone is therefore more strongly adsorbed than 2-aminoanthraquinone. The behaviour of the α-compound is not so readily understandable. Although the chelation in 1-hydroxyanthraquinone is much stronger than in 1-aminoanthraquinone, the hydroxy compound is much more strongly adsorbed on alumina than the amine; further 1-hydroxyanthraquinone is more strongly adsorbed than 2-aminoanthraquinone. These observations can only be explained by salt formation between the hydroxy compound and alumina.

Experimental

Chromatographic tubes of two different sizes were used. The smaller was 32 cm. long and of internal diameter 1·2 cm.; and the larger was 45 cm. long and of internal diameter 2 cm.

Materials.—Alumina, Type H (80–100 mesh), supplied by Peter Spence & Sons Ltd., was used throughout. Dry, redistilled benzene was used for adsorption and development.

Anthraquinone obtained from Shalimar Tar Products (1935) Ltd. was purified by sublimation and crystallization from acetic acid. 1- and 2-Aminoanthraquinones, 1 : 4-, 1 : 5- and 2 : 6-diaminoanthraquinones were commercial samples, which were purified by chromatography before use. A solution of the substance in benzene was passed through a column of alumina,

and the chromatogram developed with benzene. It was found that each of the technical aminoanthraquinones separated into a major band and several minor bands. Thus the presence of ten other constituents in technical 1-aminoanthraquinone was indicated; the identification of these constituents and the absorption spectra of the pure mono- and diaminoanthraquinones will form the subject of a later communication. The major band in each case was eluted, passed again through alumina to ensure chromatographic homogeneity, and the benzene solution so obtained was used for the subsequent study of the chromatographic behaviour of the aminoanthraquinone.

A commercial sample of 1 : 4 : 5 : 8-tetraminoanthraquinone was crystallized from alcohol, when dark navy blue needles with a red-brown metallic lustre were obtained. The substance was dissolved in benzene, passed through alumina and developed with benzene. The greenish blue band of the tetramine passed through, leaving a slight pink colouration at the top. This tetramine solution was rechromatographed and used.

N-*Methyl*-1-*aminoanthraquinone*.—Duranol Red G (I.C.I.; 80 g.), available as a paste, was boiled with 5% hydrochloric acid (800 c.c.) and filtered. The precipitate was washed acid-free and dried (17 g.); after shrinking at 130° and softening at 143°, the product melted at 148–51°. Two crystallizations from acetic acid gave shining orange-red needles, m.p. 168° (Ullmann and Fodor,[18] m.p. 170° corr.) (Found: N, 5·8. Calc. for $C_{15}H_{11}NO_2$: 5·9%). This product was dissolved in benzene and passed through alumina, when a red-violet passing band of N-methyl-1-aminoanthraquinone and a dark brown band at the top were obtained. The red-violet band was eluted with benzene, rechromatographed, and used.

1 : 4-*Bis-methylaminoanthraquinone*.—Duranol Brilliant Blue G (I.C.I.; 20 g.), available as a fine powder, was dispersed in water (500 c.c.) and concentrated hydrochloric acid added till a precipitate was obtained. The acidic solution was filtered, the precipitate suspended in water (100 c.c.), and neutralized with sodium carbonate. The blue precipitate was collected, dried and dissolved in benzene. The benzene solution was passed through alumina, when 1 : 4-bis-methylaminoanthraquinone passed through as the major greenish blue band, leaving a bluish-violet, a red-violet and a strongly adsorbed reddish blue band on the column. The eluent was concentrated, when deep blue needles of 1 : 4-bis-methylaminoanthraquinone, m.p. 221°, separated (Found: N, 10·8. $C_{16}H_{14}N_2O_2$ requires N, 10·5%).

1 : 8-*Diaminoanthraquinone*.—Commercial anthraquinone-1 : 8-disulphonic acid (20 g.) was dissolved in aquecus sodium carbonate (7·5 g. in 500 c.c.

water), and sodium chlorate (60 g.) added. The mixture was heated to reflux under stirring, and concentrated hydrochloric acid (60 c.c.) was slowly added during 30 mins. The mixture was refluxed for two hours, cooled, and the product filtered. Crystallization from toluene gave yellow needles of 1 : 8-dichloroanthraquinone (6 g.), m.p. 202° (Ullmann and Knecht,[19] m.p. 202°). 1 : 8-Dichloroanthraquinone (2 g.), *p*-toluenesulphonamide (3·6 g.; 3 mols.), anhydrous sodium acetate (1·8 g.) and copper acetate (0·2 g.) in amyl alcohol were heated under reflux for 24 hours. The solution was then cooled, filtered, and the precipitate washed with hot water and dried (3·94 g.). Crystallization from toluene gave orange-yellow needles of 1 : 8-bis-*p*-toluenesulphonamidoanthraquinone, m.p. 264–264·5° (Found: N, 5·1; S, 12·0. $C_{28}H_{22}N_2O_6S_2$ requires N, 5·1; S, 11·7%). The sulphonamide (1·5 g.) was dissolved in concentrated sulphuric acid (25 c.c.) and heated on a water-bath for an hour. The solution was drowned in ice, neutralized with caustic soda, and the precipitate filtered. This product was dried, dissolved in benzene, and passed through alumina before use. 1 : 8-Diaminoanthraquinone crystallized from benzene in dark red needles, m.p. 263–64° (Noelting and Wortmann,[20] m.p. 262°).

1 : 2-*Diaminoanthraquinone* was obtained by the ammonolysis of 1-aminoanthraquinone-2-sulphonic acid, prepared by the sulphonation of 1-aminoanthraquinone with a mixture of 20% oleum and 98% sulphuric acid at 80–120°. The product crystallized from nitrobenzene in dark violet brown needles, m.p. 300° (Ullmann and Medenwald,[21] violet needles, m.p. 303–04° corr.). A benzene solution was passed through alumina, and the scarlet band of 1 : 2-diaminoanthraquinone eluted with benzene, rechromatographed, and used.

1 : 4 : 5-*Triaminoanthraquinone*.—Caledon Red ×5 B (I.C.I.; 1 : 4 : 5-tribenzamidoanthraquinone) was hydrolysed by heating with sulphuric acid on a water-bath for an hour. The amine crystallized from aqueous pyridine in dark brown needles, m.p. 256° (F.P. 811, 479, m.p. 256–57°). A benzene solution was chromatographed, and the red-violet band of the triaminoanthraquinone eluted with benzene and used.

N-Methyl-2-aminoanthraquinone.—This was prepared according to the method of Ullmann and Medenwald.[21] The substance crystallized from dilute acetic acid in ruby-red needles, m.p. 221–22° (Ullmann and Medenwald,[21] m.p. 226–27° corr.).

Benzamidoanthraquinones.—Both 1- and 2-benzamidoanthraquinones were prepared by heating the corresponding aminoanthraquinone with a slight excess of benzoyl chloride in nitrobenzene solution. 1-Benzamido-

anthraquinone crystallized from nitrobenzene in yellowish brown needles, m.p. 253° (Reverdin,[22] blackish needles, m.p. 246°). 2-Benzamidoanthraquinone crystallized in yellow needles, m.p. 228° (Reverdin,[22] m.p. 227°).

N-Methyl-1-benzamidoanthraquinone was prepared by boiling a solution of N-methyl-1-aminoanthraquinone (1 g.) in benzoyl chloride (5 g.) for 2 hours. On cooling and pouring into water, the product was collected, washed successively with sodium carbonate solution, hydrochloric acid and water, and crystallized from dilute acetic acid. The orange-red needles had m.p. 193–193·5° (Found: N, 4·2. $C_{22}H_{15}NO_3$ requires N, 4·1%). N-Methyl-2-aminoanthraquinone was benzoylated in pyridine solution.[23] N-Methyl-2-benzamidoanthraquinone crystallized in bright orange-yellow needles, m.p. 172° (Bradley and Leete,[23] 171–72°).

TABLE II

Colour of anthraquinone derivatives in benzene solution and on alumina

No.	Substance	Colour	
		In benzene	On alumina
1	Anthracene	Colourless	Colourless
2	Anthraquinone	Pale yellow	Colourless
3	1-Aminoanthraquinone	Orange-red	Red
4	2-Aminoanthraquinone	Yellow	Yellow
5	1:2-Diaminoanthraquinone ..	Yellow-brown	Scarlet
6	1:4-Diaminoanthraquinone ..	Royal-purple	Red-violet
7	1:5-Diaminoanthraquinone ..	Orange	Red
8	1:8-Diaminoanthraquinone ..	Flame-red	Pink
9	2:6-Diaminoanthraquinone ..	Light yellow	Scarlet
10	1:4:5-Triaminoanthraquinone ..	Violet	Red-violet
11	1:4:5:8-Tetraminoanthraquinone ..	Blue	Greenish-blue
12	N-Methyl-1-aminoanthraquinone ..	Magenta	Red-violet
13	N-Methyl-2-aminoanthraquinone ..	Yellow	Pink
14	1:4-Bis-methylaminoanthraquinone ..	Blue	Greenish-blue
15	1-Benzamidoanthraquinone	Yellow	Yellow
16	2-Benzamidoanthraquinone	Yellow	Yellow
17	N-Methyl-1-benzamidoanthraquinone	Orange	Pink
18	N-Methyl-2-benzamidoanthraquinone	Yellow	Pink
19	1-Hydroxyanthraquinone	Yellow	Red-orange
20	2-Hydroxyanthraquinone	Yellow	Orange

Chromatographic behaviour of the aminoanthraquinones.—The smaller tube was normally used. The column was filled with alumina up to a height of 25 cm. by the slurry method, and when there was a steady flow of benzene through the column, a mixture (1 : 1 ; 5 c.c.) of the solutions (20 mg. in 20–30 c.c.) of any two substances was passed. The column was then developed with 50–100 c.c. of benzene, when two zones separated and were identified by their colour on alumina. Table II gives the colour of the aminoanthraquinones in benzene solution and on alumina. By studying the behaviour of these aminoanthraquinones, two at a time, the relative order of adsorbability was determined. The aminoanthraquinones and their derivatives separate easily from benzene solution on alumina, so that by using a longer column (*e.g.*, 45 cm.) it is possible to obtain the separation of eight aminoanthraquinones on the column as eight distinctly coloured bands.

Chromatographic separation of hydroxy- and aminoanthraquinones.—A benzene solution containing 1- and 2-hydroxy- and 1- and 2-aminoanthraquinones (10 mg. each) was passed through a column of alumina and developed with benzene. The hydroxyanthraquinones were strongly adsorbed at the top, and the aminoanthraquinones passed through. 1-Hydroxyanthraquinone was less strongly adsorbed than the 2-isomer. The two hydroxyanthraquinones did not separate with a clear white zone between the two, but formed two consecutive bands. They moved very slowly on the alumina column and could not be completely eluted even with alcohol or pyridine, alcoholic hydrochloric acid being necessary for the purpose.

Summary

The relation between chemical constitution and chromatographic adsorbability of a series of aminoanthraquinones and their derivatives has been investigated. Of the various types of interaction of which alumina appears to be capable in the process of adsorption, the most important is hydrogen bonding between alumina and one or more proton-donor groups in the adsorptive. When anthracene, anthraquinone and a series of aminoanthraquinones and their derivatives are chromatographed on alumina, using benzene as solvent for adsorption and development, the strength of adsorption is in the following increasing order: anthracene, anthraquinone, N-methyl-1-aminoanthraquinone, 1-benzamidoanthraquinone, 1 : 4-bis-methylaminoanthraquinone, 1-aminoanthraquinone, 1 : 5-diaminoanthraquinone and N-methyl-2-aminoanthraquinone, 1 : 8-diaminoanthraqunione, N-methyl-1-benzamidoanthraquinone and N-methyl-2-benzamidoanthraquinone, 2-aminoanthraquinone, 1 : 4-diaminoanthraquinone, 1 : 4 : 5-triaminoanthraquinone, 1 : 2-diaminoanthraquinone, 1 ; 4 ; 5 : 8-tetraminoanthraquinone, 2 : 6-diamino-

anthraquinone. The relative adsorption affinities are explained in terms of chelation between NH_2 and CO groups, resonance interaction between NH_2 and CO groups, the ability of amide groups to form hydrogen bonds, and the electron-repulsive effect of methyl groups.

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CHELATION IN AZOPHENOLS IN RELATION TO CHROMATOGRAPHIC ADSORBABILITY ON ALUMINA

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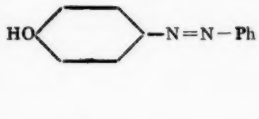
In the course of work on the action of diazonium salts on citrinin it was observed that 4-benzeneazoresorcinol was more strongly adsorbed on alumina than 2:4- or 4:6-bisbenzeneazoresorcinol, and that 6-benzeneazo-4-methylresorcinol was more strongly adsorbed than 2-benzeneazo-4-methylresorcinol.[1] These effects were ascribed to chelation between the azo and *o*-hydroxyl groups, and the present paper records a more detailed study of the chromatographic behaviour of azophenols in relation to the number and position of hydroxyl and azo groups.

Coupling of phenol

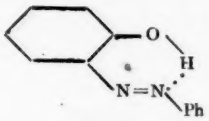
Bamberger showed in 1900 that when phenol is coupled in alkaline solution with diazotized aniline the main product (about 99%) is *p*-hydroxyazobenzene (I), m.p. 154°; the accompanying *o*-hydroxyazobenzene (II), m.p. 82·5–83°, was separated by steam distillation and further purification through the copper salt.[2] The volatility in steam and the lower m.p. of the *o*-compound are due to chelation of the hydroxyl and azo groups. For the same reason it is possible to separate the *o*- and *p*-isomers by chromatographic adsorption on alumina. It may be assumed that the forces responsible for the adsorption of azophenols on alumina are (*a*) hydrogen bonding between hydroxyl in the azophenol and oxygen in alumina, (*b*) hydrogen bonding between the hydroxyl or azo group in the azophenol and a hydroxyl group in alumina, and (*c*) electron-donor and electron-acceptor interaction between the azo group and aluminium. Chelation in *o*-hydroxyazobenzene renders both the hydroxyl and the azo group less effective for bonding with alumina in comparison with *p*-hydroxyazobenzene.

When the crude dye obtained by coupling phenol with a molar proportion of diazotized aniline was chromatographed on alumina, using benzene as solvent and developer, three bands appeared: top, orange-yellow; middle, reddish orange; and bottom, yellow. By elution with benzene *o*-hydroxyazobenzene, 2:4-bisbenzeneazophenol, and *p*-hydroxyazobenzene were re-

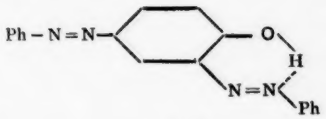
covered successively from the percolate: the respective yields were 1·1, 1 and 97·9 %. *p*-Hydroxyazobenzene is more strongly adsorbed than 2:4-bisbenzeneazophenol, notwithstanding the presence of an additional azo group in the latter compound. In *p*-hydroxyazobenzene (I) both



(I)



(II)



(III)

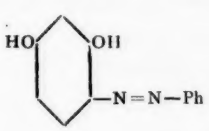
the hydroxyl and azo groups are effective in adsorption on alumina; in the disazo dye (III) only one azo group is effective, because of chelation between the second azo group and the *o*-hydroxyl.

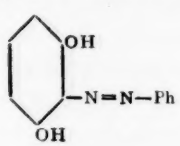
Coupling of resorcinol

Baeyer and Jager[3] first prepared mono-benzeneazoresorcinol, m.p. 166°. Typke[4] isolated two azo compounds in the reaction between resorcinol and benzenediazonium chloride: "*α*-dioxyazobenzene", m.p. 161°, and "*β*-dioxyazobenzene", m.p. 215°. The latter was given the formula $C_{12}H_{10}O_2N_2$ on the basis of its carbon and hydrogen analysis, and was considered to be 2-benzeneazoresorcinol. Typke's "*β*-dioxyazobenzene" was probably 2:4- or 4:6-bisbenzeneazoresorcinol, since the carbon and hydrogen values for both mono- and bisbenzeneazoresorcinol are very nearly the same: $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7; N, 13·1%; and $C_{18}H_{14}O_2N_4$ requires C, 67·9; H, 4·4; N, 17·6%; Typke's figures were C, 67·0; H, 4·9. The m.p. of "*β*-dioxyazobenzene", 215°, is also very near those of 4:6- and 2:4-bisbenzeneazoresorcinols (215° and 221° respectively).

Will and Pukall[5] found that in the reaction between resorcinol and benzenediazonium chloride 4-benzeneazoresorcinol (IV) constituted the main product, but the isomeric 2-benzeneazoresorcinol (V) was also formed in small quantities. From 700 g. of the crude monoazo dye, 35 g. of the 2-azo compound (V) was isolated. They could not isolate (V) in pure crystalline form, but separated the diethyl ethers of (IV) and (V). Reduction of the diethyl derivative of (V) with tin and hydrochloric acid gave a compound,

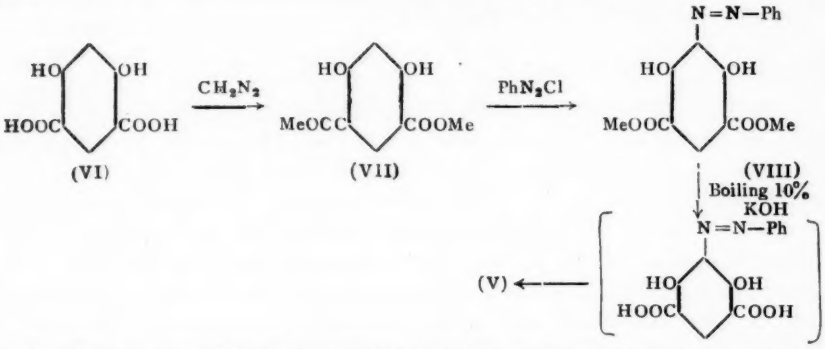
(IV)





(V)

m.p. 124°, which they believed to be 2:6-diethoxyaniline. Turner[6] prepared this amine from 2-nitroresorcinol, obtained by following the unambiguous method of Kauffmann and De Pay,[7] and found that it melted at 57°. Vorozhtozov and Gorkov[8] also observed the formation of (V) simultaneously with (IV). By methylating crude 4-benzeneazoresorcinol, Bechhold[9] obtained the dimethyl ether of (IV), m.p. 92°, and from the mother-liquor after crystallization he isolated a product, m.p. 96–97°, which he considered to be the dimethyl ether of (V). 2-Benzeneazoresorcinol (V) thus remains an unknown substance and its preparation was therefore undertaken by the following unambiguous route. When the acid (VI) was coupled with diazotized aniline, coupling was accompanied by decarboxylation, and the main product was 2:4-bisbenzeneazoresorcinol-6-carboxylic acid. The ester (VII)

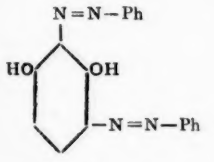


of the dicarboxylic acid (VI), obtained during carboxylation of resorcinol[10] with potassium bicarbonate in glycerine at 135°, was prepared by treatment with two moles of diazomethane in ether at 0°. The ester (VII) coupled smoothly with diazotized aniline to the 2-benzeneazo derivative (VIII), which on further treatment with 10% boiling caustic potash solution gave (V), crystallizing from alcohol in slender yellow needles, m.p. 159°; the 2-benzeneazo derivative (IX) of resorcinol-4:6-dicarboxylic acid (VI) was not isolable under these conditions of saponification, since decarboxylation to (V) took place. Although (V) is yellow in colour in contrast to (IV) which is bright orange, both (IV) and (V) give almost similar colourations with concentrated sulphuric acid and 2N aqueous caustic soda. Unlike its isomer (IV), (V) is volatile in steam and is less readily soluble in alkalis than the *p*-compound (IV). This moderation in the hydroxylic properties of (V) in comparison with (IV) enabled their separation subsequently.

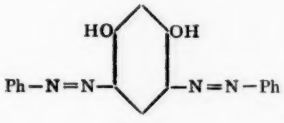
Quantitative separation of (V) from (IV) was possible by chromatography. When a solution of (IV) and (V) in chloroform was chromato-

graphed on an alumina column, it was found that (IV) appeared at the top of the column, being strongly adsorbed, while (V) was very weakly adsorbed and was recovered from the yellow percolate. The weak adsorption of (V) was apparently the result of the azo group sandwiched between the two hydroxyl groups acting as a receptor for two hydrogen bonds, so that neither of the hydroxyl groups is fully available for hydrogen bonding with the adsorbent; in (IV) the 2-hydroxyl chelates with the azo group, leaving the 4-hydroxyl free for hydrogen bonding with alumina, and (IV) is therefore more strongly adsorbed than (V). The behaviour of azoresorcinols in chromatography was found useful in separating other mixtures, and the strength of adsorption afforded a measure of the extent of chelation in azophenols. When a solution of the dimethyl ether of (IV) in chloroform was chromatographed on alumina it was very weakly adsorbed, and a mixture of the dimethyl ethers of (IV) and (V) could not be separated.

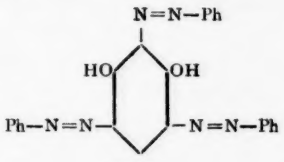
2:4-Bisbenzeneazoresorcinol (X), 4:6-bisbenzeneazoresorcinol (XI) and 2:4:6-trisbenzeneazoresorcinol (XII) were prepared by known methods: (X) by coupling resorcinol with two moles of diazotized aniline in presence of sodium carbonate,[10] and (XI) and (XII) by coupling with two or three



(X)



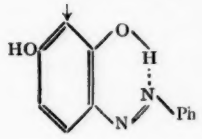
(XI)

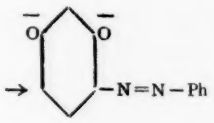


(XII)

moles of diazonium salt in caustic soda solution.[11,12] The coupling of resorcinol with 1 mole of benzenediazonium chloride at a pH of about 7 gives 4-benzeneazoresorcinol; chromatography has shown the absence of the 2-azo compound. Resorcinol couples so readily that even with 1 mole of benzenediazonium chloride about 10% of a disazo dye is formed. If coupling with 2 moles of diazonium component is carried out at pH 5–8, the main product is 2:4-bisbenzeneazoresorcinol. 4-Benzeneazoresorcinol (IV) is first formed and the entry of the second azo group into the 2-position is due to the chelation indicated in (IV A) as a result of which one of the Kekule

(IV A)





(IV B)

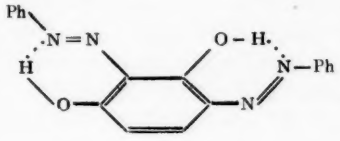
structures makes a larger contribution to the resonance of the benzene ring; coupling then takes place at the end of the double bond attached to the hydroxylated carbon atom. Under strongly alkaline conditions the hydrogen bond is broken, and coupling takes place, as in resorcinol itself, in the position *o*, *p* to the two hydroxyl groups,[13] as indicated in (IV B).

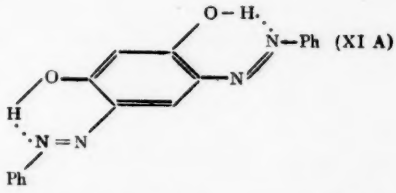
4-Benzeneazoresorcinol (IV) was more strongly adsorbed on alumina than either of the bisazo compounds. A mixture of (X) and (XI) dissolved in chloroform separated readily on alumina, (XI) appearing in the upper part of the column; (X) was very weakly adsorbed, being eluted by chloroform. When a solution of 2-benzeneazoresorcinol (V) and (X) in chloroform was chromatographed on alumina, two bands appeared, (V) constituting the upper yellow-orange band and (X) the lower orange-red band; elution with chloroform gave (X) and (V) successively in the percolate. The stronger adsorption of (V) in comparison with (X) shows that in (X) each hydroxyl group is strongly chelated with an azo group, and that in (V) the chelation of two hydroxyl groups with a single azo group is relatively weak, although it is sufficiently strong to render (V) much less strongly adsorbed than (IV) in which one hydroxyl group is completely free for hydrogen bonding with alumina. When, however, a solution of (V) and 4: 6-bisbenzeneazoresorcinol (XI) in chloroform was chromatographed it was observed that the latter was more strongly adsorbed than (V). Thus, the order of decreasing adsorbability was (IV), (XI), (V) and (X).

The behaviour of the azoresorcinols in chromatography is in contrast to the oehaviour of the azo dyes of the usual types used in dyeing wool and cotton, which were examined by Ruggli and Jensen[14] and in which the adsorbability increased with the number of azo groups. The azo groups were the determining factor in the soluble dyes containing sodium sulphonate groups, studied by Ruggli and Jensen, but the hydroxyl groups also play a part in the adsorption of the azoresorcinols. In (IV), which can be represented by the chelated structure (IV A), one hydroxyl group is free and active in adsorption; in (X) both the hydroxyl groups are chelated with the azo groups as indicated in (X A), and therefore much less active in hydrogen bonding with alumina; (IV) in consequence is more strongly adsorbed than (X). The behaviour of (X) and (XI) in chromatography indicates that (X) is more strongly chelated than (XI). This is in conformity with Baker's observation, based on the differences in physical properties, that intramolecular hydrogen bond formation is much greater in 2: 4-diacetylresorcinol (XIII) than in the 4: 6-isomer (XIV). He suggested that the fixation of one of the two Kekule structures for the benzene ring favoured

dual chelation in (XIII), but not in (XIV).[15] Bond fixation in ring structures has not found adequate support in experimental evidence or theoretical considerations, and attempts are being made to explain such facts as the diazonium coupling of β-naphthol solely in the 1-position and of 5-hydroxyindane mainly in the 6-position on other grounds, which do not postulate a static system involving the fixation of bonds and which take into account the relative stability of the activated complexes, the number of resonance structures in which the favoured position is activated, and the electron densities at the

(X A)

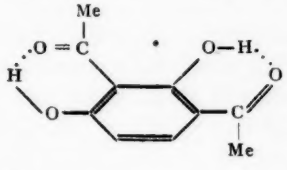


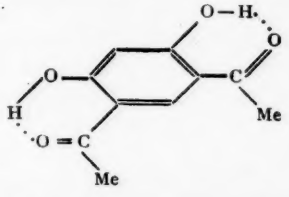


(XI A)

sites available for attack by a given reagent.[16] Pauling has suggested that the conjugated system in the chelate rings in (XIII) increases the ionic character of the O—H bond, as well as the negative charge on the carbonyl oxygen, and therefore the strength of the hydrogen bond.[17] In the chelate structure (X A) for 2:4-bisbenzeneazoresorcinol each of the chelate rings contains two double bonds, while in structure (XI A) for the 4:6-compound one chelate ring cannot implicate a double bond of the benzene ring in either of the two Kekule structures. The " additional double bond stabilization "[18] in (X A) increases the resonance stabilization of the chelate rings

(XIII)





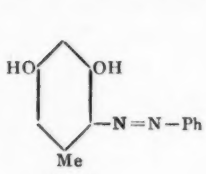
(XIV)

in (X A) in comparison with (XI A). As a result one hydroxyl group in 4:6-bisbenzeneazoresorcinol (XI) is partially free for hydrogen bonding with alumina, and (XI) is more strongly adsorbed than 2:4-bisbenzeneazoresorcinol (X).

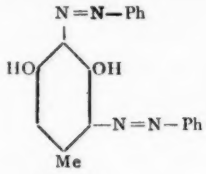
Coupling of 4-methylresorcinol and orcinol

Orcinol[19] is known to give two azo derivatives, 4-benzeneazo-5-methylresorcinol (XV) and a disazo derivative, m.p. 229°, which may be (XVI) or

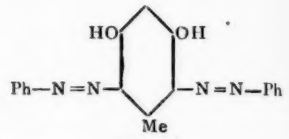
(XVII). The orientation of this disazo derivative was not determined. The γ- or 2-position in 5-substituted resorcinols has considerable reactivity



(XV)



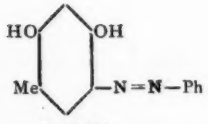
(XVI)



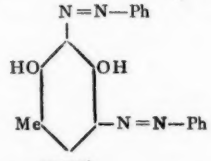
(XVII)

in reactions such as carboxylation and the Fries rearrangement. On examining the azo dyes formed during coupling of orcinol with benzenediazonium chloride (one mole) 2-benzeneazo-5-methylresorcinol could not be isolated. When orcinol was coupled with diazotized aniline at pH 5–8, the monoazo derivative (XV) was accompanied by a disazo compound, melting at 224°. The dye obtained by coupling orcinol with diazotized aniline in dilute caustic soda solution crystallized from acetic acid in chocolate brown needles, m.p. 229°, and was also a disazo derivative of orcinol. The m.p. corresponded with the disazo derivative obtained by Simon.[19] Comparison of the absorption spectra and mode of formation of the bisazo derivatives of orcinol, m.p. 224 and 229°, with those of 2:4- and 4:6-bisbenzeneazoresorcinols conclusively showed that they were 2:4-bisbenzeneazo-5-methylresorcinol (XVI) and 4:6-bisbenzeneazo-5-methylresorcinol (XVII) respectively. The behaviour of (XV), (XVI) and (XVII) in chromatographic adsorption on alumina was similar to that of the corresponding azo derivatives of resorcinol, the order of decreasing adsorbability being (XV), (XVII) and (XVI).

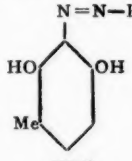
On coupling 4-methylresorcinol with diazotized aniline 6-benzeneazo-4-methylresorcinol (XVIII) and 2:4-bisbenzeneazo-6-methylresorcinol (XIX) were obtained. The 2-benzeneazo derivative (XX) could not be obtained



(XVIII)



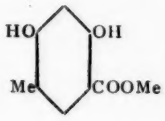
(XIX)



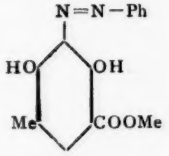
(XX)

by direct coupling, and was prepared by coupling the methyl ester (XXII) of 4-methylresorcinol-6-carboxylic acid (XXI) with benzenediazonium chloride and treating the azo dye (XXIII) with 10% boiling alcoholic caustic potash solution. Both 2-benzeneazoresorcinol (V) and the dye (XX) are

yellow in colour, volatile in steam, and insoluble in 5% sodium bicarbonate solution, while 4-benzeneazoresorcinol (IV) and 4-benzeneazo-6-methylresorcinol (XVIII) are bright orange in colour, non-volatile in steam and soluble in 5% sodium bicarbonate solution. The 2-azo derivatives also melt at lower temperatures than the corresponding 4-azo compounds. The behaviour of (XVIII), (XIX) and (XX) in chromatographic adsorption on alumina was similar to that of the corresponding azo derivatives of resorcinol,



(XXII)

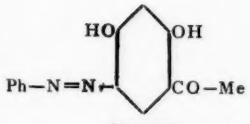


(XXIII)

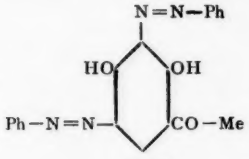
the order of decreasing adsorbability being (XVIII), (XX) and (XIX).

Coupling of resacetophenone and 2-acetylresorcinol

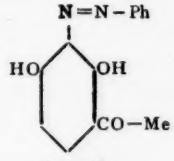
When resacetophenone was coupled with diazotized aniline (one mole) at pH 5–7, using sodium acetate, coupling was not noticed; at pH 8–9, using sodium acetate and sodium carbonate, the product obtained was a mixture of a monobenzeneazoresacetophenone, m.p. 192°, and a disazo derivative (XXV). At pH 11–13, the same products were obtained. With excess of aniline (4 moles) 3:5-bisbenzeneazoresacetophenone (XXV) was obtained in nearly quantitative yield. Under no set of conditions was the displace-



(XXIV)



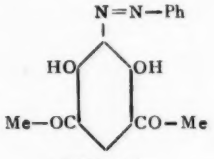
(XXV)



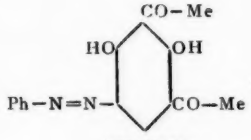
(XXVI)

ment of the acetyl group observed. The structure of the monobenzeneazoresacetophenone can be either (XXIV) or (XXVI), since γ-substitution in resacetophenone has been frequently observed.[15,20] Both (XXIV) and (XXVI) were not formed, since only one monoazo dye could be isolated. The constitution of the monoazo dye as (XXIV), and not (XXVI), was evident from its similarity with 4-benzeneazoresorcinol (IV) in chromatographic behaviour. It was also independently proved by carrying out the Fries rearrangement on the diacetyl derivative. The product was found to be identical with 2:4-diacetyl-6-benzeneazoresorcinol (XXVIII), while the Fries

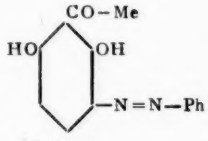
reaction on the diacetate of (XXVI) would have yielded 4:6-diacetyl-2-benzeneazoresorcinol (XXVII). The dyes (XXVII) and (XXVIII) were prepared for comparison by coupling 4:6-diacetylresorcinol and 2:4-diacetylresorcinol respectively with benzenediazonium chloride. The complete failure of 4-acetylresorcinol and methyl β-resorcylate (see later paper) to couple in the 2-position shows the relative weakness of the hydrogen bond between the carbonyl (or carbomethoxy) and adjacent hydroxyl groups in comparison with the chelation in *o*-hydroxyazobenzenes, as well as a marked difference in the influence of such chelation on the Fries rearrangement and



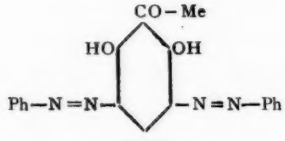
(XXVII)



(XXVIII)



(XXIX)



(XXX)

on diazonium coupling. The mechanism of diazonium coupling consists in the attraction of the diazonium cation to a site of high electron density, and the *para*-position in a phenol is the favoured position for coupling; thus phenol gives 98% of *p*-hydroxyazobenzene and only 1% of the *o*-compound. In resacetophenone and methyl β-resorcylate hydrogen bonding does not materially influence the electron density at the second position *o-p* to the two hydroxyl groups, and diazonium coupling therefore takes place at this readily accessible or unhindered position. The mechanism of the Fries migration is relatively complex, and unlike the coupling of phenol with diazonium salts, the Fries reaction on phenyl acetate gives a mixture *o*- and *p*-hydroxyacetophenone in relative proportions dependent on the solvent, the quantity of aluminium chloride, and in particular the temperature. Baker has shown that the Fries reaction on resacetophenone 4-acetate gives a mixture of 2:4- and 4:6-diacetylresorcinol, and the Claisen rearrangement of the 4-allyl ether gives 85% of 3-allylresacetophenone.[15]

2-Acetylresorcinol gave 2-acetyl-4-benzeneazoresorcinol (XXIX) and the disazo derivative (XXX) when coupled with diazotized aniline. When coupling was carried out at pH 5–7, (XXIX) was obtained in almost quanti-

tative yield even with 2·5 moles of diazotized aniline, and the formation of (XXX) required a considerably higher pH. There was no displacement of the acetyl group under any conditions. A mixture of the dyes (XXIX) and (XXX) could be easily separated by chromatography on alumina; the former was more strongly adsorbed, again demonstrating the weakness of the electron-donor character of carbonyl oxygen compared to azo nitrogen in the formation of an intramolecular hydrogen bond.

Experimental

Coupling of phenol with diazotized aniline

Aniline (4·65 g.; 0·05 mole) was diazotized at 0° by means of hydrochloric acid (33%; 11·5 c.c.) and sodium nitrite (3·2 g.) and the diazonium solution was added to a mechanically stirred solution of phenol (4·7 g.; 0·05 mole) in aqueous sodium carbonate (8%; 160 c.c.) cooled with ice and salt. The reaction mixture was stirred for one hour, acidified, and the yellow dye filtered, washed and dried (8·5 g.). A solution of the crude dye (0·7 g.) in benzene (70 c.c.) was chromatographed on standardized alumina. Three bands appeared: an orange-yellow band at the top, a red-orange band in the middle and a yellow band at the bottom. On eluting the chromatogram with benzene the bottom band was eluted and a yellow crystalline substance was recovered from the percolate (0·0076 g.). On crystallization from alcohol and sublimation at 0·02 mm. pressure, orange crystals of *o*-hydroxyazobenzene (II), m.p. 82·5–83°, were obtained. By cutting out the reddish orange middle zone and extracting the alumina with boiling alcohol the dye obtained (0·007 g.) crystallized from alcohol in brown needles, m.p. 131°. This was 2:4-bisbenzeneazophenol (III). By separating the orange-yellow zone of alumina at the top and boiling with alcohol a yellow dye was obtained, which on crystallization from alcohol and sublimation gave orange-yellow crystals of *p*-hydroxyazobenzene (I), m.p. 155°. Thus the order of decreasing adsorbability was (I), (III) and (II).

Dimethyl resorcinol-4:6-dicarboxylate (VII)

A suspension of resorcinol-4:6-dicarboxylic acid, m.p. 312° (dec.) (2 g.), in ether (50 c.c.) was treated with an ethereal solution of diazomethane (40 c.c.), obtained from nitrosomethyl urea (3·5 g.; equivalent to 0·84 g. of diazomethane; 2 mols.) at 0°. The suspension was mechanically stirred for one hour and was allowed to stand overnight at room temperature. The reaction mixture, which contained some solid crystalline material, was extracted with ether. The ether solution was then extracted with 5% aqueous

sodium bicarbonate, which removed the free acid, washed and dried over anhydrous sodium sulphate. Recrystallization from benzene of the crystalline residue obtained on evaporation of ether gave colourless prisms, m.p. 148° (Found: C, 52·8; H, 4·4. $C_{10}H_{10}O_6$ requires C, 53·1; H, 4·4%. Jois, *et al.*[21] report 147° as the m.p. of the ester). The alcoholic solution of the ester gives a red colouration with alcoholic ferric chloride.

Dimethyl 2-benzeneazoresorcinol-4: 6-dicarboxylate (VIII)

A solution of benzenediazonium chloride prepared from aniline (0·5 g.; 1·25 mols.), hydrochloric acid (33%; 1·5 c.c.) and sodium nitrite (0·35 g.) was treated with sodium acetate (2 g.) and gradually added to a solution of the dimethyl ester (VII) (1 g.) in 5% caustic soda solution (30 c.c.). During addition and thereafter for two hours the reaction mixture was mechanically stirred and the temperature maintained at 0–3°. It was then acidified with dilute hydrochloric acid and the red-orange precipitate of the dye was collected, washed and dried (1·5 g.). Crystallization from glacial acetic acid gave orange needles, m.p. 232° (Found: N, 8·5. $C_{16}H_{14}O_6N_2$ requires N, 8·5%).

2-Benzeneazoresorcinol (V)

The dimethyl ester of 2-benzeneazoresorcinol-4: 6-dicarboxylic acid (0·6 g.) was refluxed with 10% aqueous caustic potash (100 c.c.) containing a little alcohol (5 c.c.) for four hours on a steam-bath. The orange-yellow solution was filtered and on acidifying a yellow-orange precipitate was obtained (0·33 g.) which crystallized from dilute alcohol in orange-yellow needles, m.p. 159° (Found: C, 66·9; H, 4·7; N, 13·1. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7; N, 13·1%). The m.p. in admixture with a sample of 4-benzeneazoresorcinol (IV) was lowered to 137°. The substance is yellow-orange in colour in contrast to (IV) which is bright orange. Both (IV) and (V) when dissolved in alcohol give bright orange-coloured solutions. The dye (V) gives a bright orange colour with concentrated sulphuric acid as well as with 10% caustic soda solution. The dye is steam-volatile.

The diacetate prepared by heating (V) with acetic anhydride and pyridine crystallized from alcohol in orange needles, m.p. 137° (Found: C, 64·2; H, 4·6; N, 9·3. $C_{16}H_{14}O_4N_2$ requires C, 64·4; H, 4·7; N, 9·4%).

The dimethyl ether of (V) was obtained by refluxing a mixture of (V) (0·05 g.), acetone (5 c.c.) and anhydrous potassium carbonate (0·2 g.) for eight hours. The red product crystallized from dilute alcohol in lustrous red needles, m.p. 101° (Found: C, 69·0; H, 5·5; N, 11·5. $C_{14}H_{14}O_2N_2$

requires C, 69·4; H, 5·8; N, 11·6%). Bechhold[9] reports 96–97° as the m.p. of the dimethyl ether of (V).

Coupling of resorcinol with diazotized aniline; preparation of 4-benzeneazoresorcinol (IV), *2:4-bisbenzeneazoresorcinol* (X), *4:6-bisbenzeneazoresorcinol* (*XI*) *and 2:4:6-trisbenzeneazoresorcinol* (*XII*)

4-Benzeneazoresorcinol (IV) and the disazo dyes (X) and (XI) were prepared by coupling resorcinol with diazotized aniline in the known manner.[10,12] The dye (IV) crystallized from dilute alcohol in orange needles, m.p. 162°. The m.p. remained unchanged on drying at 85° in vacuum (0·02 mm.) for one hour. On crystallization from absolute alcohol, red-orange needles, m.p. 170°, were obtained. The dye dissolves in concentrated sulphuric acid and in aqueous caustic soda, forming orange solutions. The dye (X) crystallized from alcohol, or chloroform and alcohol, in red needles, m.p. 222°, while (XI) was obtained as brown needles from alcohol, m.p. 215–16° [Kostanecki[10] records 221° and 213–15° as the m.p. of (X) and (XI) respectively]. With caustic soda solution (X) gives an orange colouration, while the 4:6-isomer (XI) gives a bordeaux-red colouration. With concentrated sulphuric acid both give red-orange colourations. 2:4:6-Trisbenzeneazoresorcinol (XII) was obtained by coupling resorcinol (0·44 g.) with diazotized aniline (1·5 g.; 4 mols.) in dilute caustic soda solution (50 c.c. of 5% solution). The dye (1·4 g.) on purification and crystallization from benzene was obtained as red-brown needles, m.p. 253° (Orndorff,[12] 253°). The yield of the dye (XII) was about 25%, and the main product was (XI). The dye (XII) gives a deep violet colouration with concentrated sulphuric acid.

Behaviour of azoresorcinols in chromatography on alumina

(1) *Separation of* (*IV*) *and* (*V*) *by chromatographic adsorption.*—A solution of (IV) (0·025 g.) and (V) (0·005 g.) in chloroform (20 c.c.) was chromatographed on standardized alumina. An orange band of 0·5 cm. height was formed at the top, while a yellowish-orange percolate moved downwards. On developing with the same solvent the orange band remained adsorbed and (V) was recovered almost quantitatively from the chloroform percolate. The orange layer of alumina at the top of the column was separated and extracted with boiling alcohol, slightly acidulated with hydrochloric acid; and evaporation gave (IV). It was possible to separate (V) from (IV) when a solution of (V) and (IV) in the proportion 1 : 99 in chloroform was chromatographed on alumina. Separation of the dimethyl ethers of (IV) and (V) by chromatographic adsorption was not possible, since both were very weakly adsorbed on alumina.

(2) *Separation of (IV) and (X) by chromatographic adsorption.*—A solution of 4-benzeneazoresorcinol (IV) (0·025 g.) and 2:4-bisbenzeneazoresorcinol (0·025 g.) in chloroform (20 c.c.) was chromatographed on alumina. A scarlet band was formed at the top, while an orange percolate moved downwards. On developing with chloroform and benzene (1:1), the scarlet band remained adsorbed and (X) was recovered from the chloroform-benzene percolate. By separating the scarlet layer of alumina and boiling with alcohol, (IV) was obtained.

(3) *Separation of (X) and (XI) by chromatographic adsorption.*—A solution of 2:4-bisbenzeneazoresorcinol (X) (0·005 g.) and 4:6-bisbenzeneazoresorcinol (XI) (0·005 g.) in chloroform (15 c.c.) was chromatographed on alumina. A red-orange band separated from the orange percolate moving downwards. On developing with chloroform and benzene (1:1) the red-orange band remained adsorbed and (X) was recovered from the chloroform-benzene percolate. On separating the red-orange layer of alumina and boiling with alcohol, (XI) was recovered.

(4) *Separation of 2-benzeneazoresorcinol (V) from (X)* was also possible by chromatographic adsorption. When a solution of (V) (0·005 g.) and (X) (0·005 g.) in chloroform (10 c.c.) was adsorbed on alumina and developed with the same solvent two bands appeared: an upper yellow band and a lower orange band. The lower band on elution with chloroform gave (X), while the upper band gave (V).

(5) *Separation of (V) and (XI).*—A solution of (V) (0·005 g.) and (XI) (0·005 g.) in chloroform (10 c.c.) was chromatographed on alumina. On developing with chloroform two bands appeared: an upper red-orange band and a lower yellowish orange band. The lower band on elution with chloroform gave 2-benzeneazoresorcinol (V), while the upper red band on extracting with boiling alcohol gave (XI). Thus (XI) was more strongly adsorbed than (V).

(6) When a solution of (IV), (V), (X) and (XI), each weighing about 5 mg., in chloroform was chromatographed on alumina and the chromatogram developed with the same solvent, four bands appeared: a scarlet upper band, then a red-orange band, then a yellowish orange band, and an orange band at the bottom. Eluting with chloroform, the lowest band was found to be 2:4-bisbenzeneazoresorcinol (X). By separating the three layers of alumina and boiling with alcohol, (IV), (XI) and (V) were recovered from the first, second and third band. Thus the order of decreasing adsorbability was (IV), (XI), (V) and (X).

Coupling of resorcinol with diazotized aniline (one mole) and examination of the crude dye for the presence of 2-benzeneazoresorcinol (V)

Aniline (0·93 g.; 0·01 mole) was diazotized, and the diazonium solution, treated with sodium acetate (3·0 g.), was added at 0° to a mechanically stirred solution of resorcinol (1·1 g.; 0·01 mole) in water (50 c.c.). The reaction mixture (ρH 5–7) was stirred for half an hour and the orange precipitate filtered, washed and dried (1·7 g.) (Found: N, 13·9%). The crude dye was dissolved in chloroform and chromatographed on alumina. A scarlet band was formed at the top and a yellow orange percolate moved downwards. 4-Benzeneazoresorcinol (IV) was obtained from the orange layer of alumina at the top, which crystallized from dilute alcohol in orange needles, m.p. 162° (Found: N, 13·1. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). Evaporating off the chloroform from the percolate, a red crystalline product was obtained (0·16 g.), a part of which on crystallization from alcohol-acetic acid gave red needles, m.p. 222°, identified as (X) (Found: N, 17·6. $C_{18}H_{14}O_2N_4$ requires N, 17·6%). On rechromatographing this substance on an alumina column, the presence of 2-benzeneazoresorcinol (V) was not indicated. Examining this product for its solubility in 20% alcohol and 2% caustic soda solution in which (X) was found to be completely insoluble while (V) gave coloured solutions, the absence of (V) was confirmed.

Coupling resorcinol (0·55 g.; 0·005 mole) in 5% caustic soda solution (25 c.c.) with one mole of diazotized aniline and carrying out the chromatographic separation of the crude dye (0·75 g.), the major portion of the dye was found to be (IV). The disazo dye recovered by elution with chloroform was found to be (XI), m.p. 216° (yield 0·28 g.). On further examining this product by chromatography on alumina the presence of (V) was not indicated.

Coupling of orcinol with diazotized aniline and formation of 4-benzeneazo-5-methylresorcinol (XV), 2:4-bisbenzeneazo-5-methylresorcinol (XVI) and 4:6-bisbenzeneazo-5-methylresorcinol (XVII)

(1) Orcinol (0·5 g.) was dissolved in alcohol (10 c.c.) and water (20 c.c.) containing sodium acetate (2·2 g.) and treated with the diazonium solution obtained from aniline (0·37 g.; 1 mol.); the red-orange precipitate was filtered, washed and dried (0·65 g.) (Found: N, on the crude sample, 13·0%). On crystallization from alcohol bunches of orange needles were obtained, m.p. 224° (Found: N, 16·6. $C_{19}H_{16}O_2N_4$ requires N, 16·9%). The m.p. in admixture with (XVII) was lowered to 210°. The mother liquor on dilution with water gave a crystalline product, which on recrystallization from

dilute alcohol gave orange needles, m.p. 184° (Typke,[19] 183°) (Found: N, 12·3. $C_{13}H_{12}O_2N_2$ requires N, 12·3%).

(2) Coupling orcinol (0·25 g.) in 5% sodium carbonate solution (15 c.c.) containing sodium acetate (1 g.) with diazotized aniline (2 mols.), the dye obtained (0·5 g.) crystallized from glacial acetic acid in orange needles, m.p. 224°, identified as (XVI).

(3) Coupling orcinol (0·25 g.) in 5% caustic soda solution (20 c.c.) with diazotized aniline (2 mols.), a red-violet product was obtained (0·3 g.), which on crystallization from glacial acetic acid gave red-violet needles, m.p. 229–30° (Simon[16] records 229° as the m.p. of the bisbenzeneazo derivative of orcinol) (Found: N, 16·6. $C_{19}H_{16}O_2N_4$ requires N, 16·9%).

When a solution of (XV), (XVI) and (XVII) (each weighing about 5 mg.) in chloroform was chromatographed on alumina and the chromatogram developed by the same solvent, three bands appeared. On eluting with chloroform (XVI) was recovered from the percolate. Bands one and two gave (XV) and (XVII) respectively. Thus the order of decreasing adsorbability was (XV), (XVII) and (XVI), confirming the structures assigned to the bisbenzeneazoorcinols.

Coupling of resacetophenone with benzenediazonium chloride; formation of 5-benzeneazoresacetophenone (XXIV) and 3:5-bisbenzeneazoresacetophenone (XXV)

(1) Resacetophenone (0·3 g.) was dissolved in alcohol (15 c.c.) and water (10 c.c.) containing 2 g. of sodium acetate and treated with benzenediazonium chloride obtained from aniline (0·19 g.; 1 mol.). No sign of coupling was observed at the end of 4 hours.

(2) Resacetophenone (0·6 g.) was dissolved in water (25 c.c.) containing sodium carbonate (1·2 g.) and sodium acetate (10 g.), and treated at 0° with benzenediazonium chloride obtained from aniline (0·37 g.; 1 mol.). The red dye obtained was filtered, washed and dried (0·85 g.). On chromatographing the chloroform solution of the crude dye, a scarlet band appeared at the top of the alumina column, while an orange percolate moved downwards. The dye recovered from the chloroform percolate crystallized from glacial acetic acid in red needles, m.p. 221–22° (Found: N, 15·5. $C_{20}H_{16}O_3N_4$ requires N, 15·6%). This is 3:5-bisbenzeneazoresacetophenone (XXV). *The diacetyl derivative* of (XXV) crystallized from alcohol in red needles, m.p. 148° (Found: N, 12·8. $C_{24}H_{20}O_5N_4$ requires N, 12·6%). The dye obtained from the scarlet layer of alumina by boiling with alcohol crystallized from alcohol in orange plates, m.p. 192° (Found: N, 11·1. $C_{14}H_{12}O_3N_2$

requires N, 10·9%). *The diacetyl derivative* of (XXIV) crystallized from alcohol in orange plates, m.p. 106–107° (Found: N, 15·5. $C_{20}H_{16}O_3N_4$ requires N, 15·6%).

(3) Coupling resacetophenone (0·6 g.) in 5% sodium hydroxide solution (20 c.c.) with one mole of diazotized aniline, and carrying out the separation of the crude dye (0·9 g.) as described in the previous experiment, both (XXIV) and (XXV) were obtained.

Fries rearrangement of the diacetate of (XXIV)

The diacetate of (XXIV) (0·4 g.) was heated with freshly prepared aluminium chloride (1 g.). The temperature was rapidly raised to 120° and then gradually to 180° in 2 hours, and was maintained at this temperature for 1 hour and cooled. The reaction mass was treated with ice and hydrochloric acid, and the red product was heated with 10% caustic soda solution for 1 hour. The dye obtained on acidifying was collected, washed and dried. On purifying by means of chromatography, the red dye crystallized from alcohol in red elongated plates, m.p. 144° (Found: N, 9·7. $C_{16}H_{14}O_4N_2$ requires N, 9·4%). The m.p. was not depressed in admixture with 6-benzeneazo-2:4-diacetylresorcinol (XXVIII). Thus the rearrangement product is (XXVIII) and confirms the structure of the monobenzeneazoresacetophenone as (XXIV).

6-*Benzeneazo*-2:4-*diacetylresorcin* (*XXVIII*)

2:4-Diacetylresorcinol, prepared according to Limaye,[22] m.p. 92° (0·05 g.), was coupled with diazotized aniline (1·5 mols.). The dye crystallized from alcohol in red plates, m.p. 144° (Found: N, 9·4. $C_{16}H_{14}O_4N_2$ requires N, 9·4%).

2-*Benzeneazo*-4:6-*diacetylresorcin* (*XXVII*)

The red dye (0·2 g.) obtained by coupling 4:6-diacetylresorcinol (0·2 g.) with diazotized aniline (1·2 mols.), on crystallization from glacial acetic acid, gave orange-red needles, m.p. 202° (Found: N, 9·7. $C_{16}H_{14}O_4N_2$ requires N, 9·4%).

Coupling of 2-*acetylresorcinol with diazotized aniline and formation of* 2-*acetyl*-4-*benzeneazoresorcinol* (*XXIX*) *and* 2-*acetyl*-4:6-*bisbenzeneazoresorcinol* (*XXX*)

(1) 2-Acetylresorcinol (0·3 g.) was dissolved in alcohol (15 c.c.) and treated with the diazonium solution obtained from aniline (0·22 g.; 1·2 mols.) and sodium acetate. The orange red needles obtained after puri-

fication and crystallization from alcohol melted at 150–51° (Found: N, 10·9. $C_{14}H_{12}O_3N_2$ requires N, 10·9%).

(2) 2-Acetylresorcinol (1·0 g.) was dissolved in 2% caustic soda solution (50 c.c.) and was treated with the diazonium solution from aniline (1·52 g.; 2·5 mols.) at 0°. The reaction mixture was stirred for one hour and then acidified. The violet precipitate was filtered, washed and dried (2·2 g.). Purification by chromatography and crystallization from glacial acetic acid gave red-violet needles, m.p. 168°. On recrystallization from alcohol red-violet rods were obtained, m.p. 170° (Found: N, 15·5. $C_{20}H_{16}O_3N_4$ requires N, 15·6%). The substance dissolves in caustic soda solution with a bordeaux-red colour, characteristic of 4:6-bisazoresorcinol derivatives. With concentrated sulphuric acid it gives a deep purple colouration.

(3) Coupling 2-acetylresorcinol with diazotized aniline (3 mols.) under the conditions described in (1), the dye obtained was 2-acetyl-4-benzeneazoresorcinol (XXIX). No formation of (XXX) was noticed.

Summary

The relative adsorption affinities of monoazo derivatives of phenol and resorcinol have been explained on the basis of chelation and of the availability of hydroxyl and azo groups for interaction with alumina. Since Ruggli has shown that monoazo, disazo and trisazo dyes are adsorbed in the given increasing order of strength of adsorption, an observation of special interest, explained by chelation effects, is that *p*-hydroxyazobenzene is more strongly adsorbed than 2:4-bisbenzeneazophenol, and that 4-benzeneazoresorcinol is more strongly adsorbed than 2:4- or 4:6-bisbenzeneazoresorcinol.

When phenol is coupled with a molar proportion of diazotized aniline, *o*-hydroxyazobenzene, *p*-hydroxyazobenzene and 2:4-bisbenzeneazophenol are formed in yields of 1·1, 97·9 and 1% respectively. They are separable by chromatography on alumina, the adsorption affinity being in the following decreasing order: *p*-hydroxyazobenzene, 2:4-bisbenzeneazophenol, and *o*-hydroxyazobenzene.

2-Benzeneazoresorcinol has been prepared by coupling diazotized aniline with dimethyl resorcinol-4:6-dicarboxylate, followed by hydrolysis and decarboxylation. 4-Benzeneazoresorcinol, 4:6-bisbenzeneazoresorcinol, 2-benzeneazoresorcinol, and 2:4-bisbenzeneazoresorcinol are adsorbed on alumina in the given order of decreasing strength of adsorption. Examining the crude dye obtained by coupling resorcinol with benzenediazonium

chloride by chromatography on alumina in the light of the above observations, it is shown that, contrary to statements in the literature, there is no evidence of the formation of 2-benzeneazoresorcinol.

Although the γ- or 2-position of 5-substituted resorcinols has considerable reactivity in reactions such as carboxylation and the Fries rearrangement, the first coupling of orcinol with diazotized aniline takes place entirely in the 4-position. The second coupling takes place in the 2- or 6-position according as the pH is 5–8 or higher.

Resacetophenone couples with diazotized aniline to a mixture of 5-benzeneazo- and 3:5-bisbenzeneazoresacetophenone; the constitution of the former was shown by the Fries rearrangement of the diacetate to 2:4-diacetyl-6-benzeneazoresorcinol. The failure of resacetophenone to undergo the first coupling in the γ-position shows the weakness of the hydrogen bond between the carbonyl and adjacent hydroxyl groups, as well as a marked difference in the influence of such chelation on the Fries rearrangement and on diazonium coupling.

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RAMAN SPECTRUM OF DANBURITE

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

The Raman spectrum of danburite ($CaB_2Si_2O_8$) has been investigated by Nisi (1929, 1932). Working with a colourless transparent specimen (11 mm. × 7 mm. × 5 mm.) and the visible radiations of the mercury arc, he recorded 16 frequency shifts. It was observed that the scattered intensity in danburite was only a third of that of calcite and that the Raman spectrum was accompanied by a fairly strong continuum. In view of the complicated structure of danburite ($CaB_2Si_2O_8$) and the large number of atoms in the unit cell, it appeared that the results obtained by Nisi are incomplete and as such a study of its Raman spectrum using the Rasetti technique has been carried out by the author.

2. Experimental Details and Results

In the present study, a clear transparent specimen (1·5 cm. × 5 mm. × 5 mm.) with its natural faces 120 and $\bar{1}20$ well developed was used. The incident light was normal to the 120 face and the scattered light was normal to the $\bar{1}20$ face of the crystal. With the medium quartz spectrograph, using a fairly fine slit (·03 mm.) exposures of the order of 12 hours were found to be necessary to obtain moderately exposed spectrograms. The recorded spectrum exhibits 30 Raman lines, 14 of which have been observed for the first time [see microphotometer record (Fig. 1) and (Fig. 2 *a*)]. The frequency shifts are given in Table I along with those reported by Nisi and the observed infra-red reflection maxima (Matossi and Krueger, 1936).

As in phenacite (Narayanan, 1950), all the Raman lines are extremely sharp, and lines separated by a few wave-numbers can be distinguished. Further, as there is some similarity between the spectra of topaz and danburite, the frequency shifts of the Raman lines of topaz recorded by Krishnan (1947) have also been included in Table I (see Fig. 2 also). In both these crystals, the low frequency lines are sharper than the high frequency ones. The lines 269 and 1205 cm.$^{-1}$ reported by Nisi have not been observed

TABLE I

Observed frequency shift in cm.$^{-1}$		Infra-red maxima	Topaz (Krishnan)
Author	Nisi		
115	92		
126	124		
153			156
167			167
183	186		
193			190
209	207		
227			
246	242		241
	269		269
296	289		287
313			317
348	342		335
			362
376	371		374
421	422	*424*	405
444			441
462			459
480		479	490
			520
564			550
609			558
627		*625*	650
		697	705
771			770
865			850
899	884	883	874
			898
926		910	920
			934
949			940
971	970	970	
		1009	
		1045	
1107	1110	1099	985
1171	1158	*1139*	1162
1558	1205		
1581			1235–1280
			1355–1435
			3636
			3649

in the present investigation. It is likely that both these lines are absent in the orientation used by the author and mentioned above.

3. INFRA-RED SPECTRUM

The infra-red spectrum of danburite has been investigated by Matossi and Krueger (1936) and they have reported reflection maxima corresponding to 8·78, 9·10, 9·57, 9·91, 10·31, 10·74, 11·33, 14·35, 16·0, 20·9 and 23·6 μ.

These infra-red reflection maxima have also been listed in column 3 of Table I, the strong ones being shown in italics.

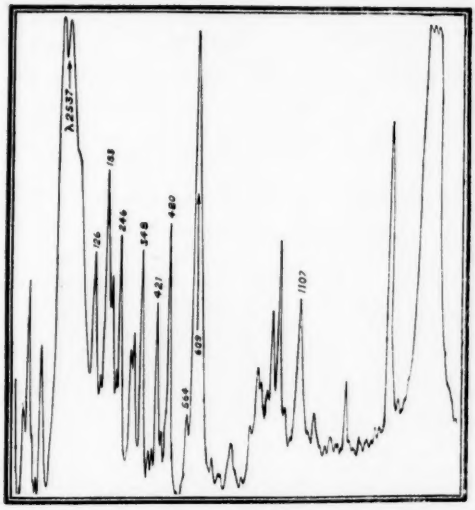

FIG. 1. Microphotometer Curve of the Raman Spectrum of Danburite

4. DISCUSSION

The crystal structure of danburite has been analysed by Dunbar and Machatschki (1930) and it is similar to that of topaz. Danburite belongs to the orthorhombic class and the space group is V_h^{16} and there are four molecules in the unit cell. In the lattice, both silicon and boron nuclei lie within tetrahedral groups of oxygen atoms. These tetrahedral groups are linked by their corners, each oxygen atom being common to two tetrahedra. Thus 8 out of the 32 oxygen atoms in the unit cell occupy special positions and are on reflection planes. The character table for the unit cell may easily be written out and it is seen that 78 frequencies are permitted in Raman effect and 54 in infra-red absorption. The presence of a centre of symmetry makes the infra-red maxima and Raman shifts complementary and no coincidence can be expected. However, it is found that 4 of the observed infra-red maxima have almost the same frequency as the observed Raman lines. It may be accidental, as the infra-red frequencies given here correspond to reflection maxima. Also, the difference between the theoretically expected number of shifts and that actually observed may arise because of two reasons. It is likely that more than one mode has very nearly the same frequency and/or those modes which involve a movement of the boron atoms

may not have appreciable intensity. For a more detailed analysis of the spectrum, a detailed investigation of the effect of crystal orientation on intensity and state of polarisation of the Raman lines is necessary.

The author is much indebted to Prof. Sir C. V. Raman for the loan of a specimen of danburite and to Prof. R. S. Krishnan for his help and encouragement.

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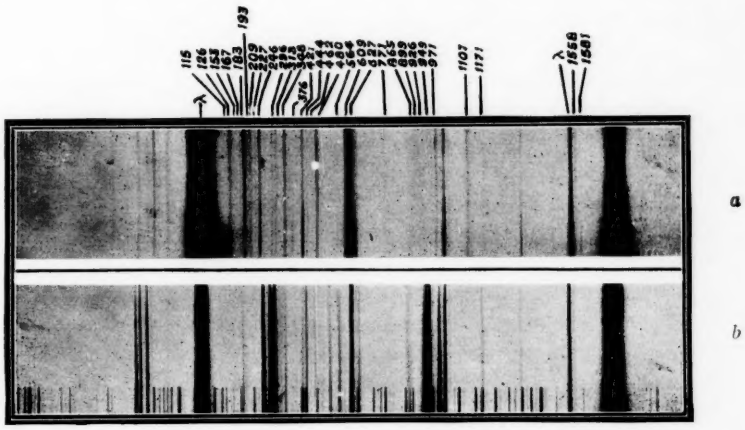

Fig. 2 (*a*). Raman Spectrum of Danburite.
Fig. 2 (*b*). ,, ,, Topaz.

THE AGEING OF BORDEAUX MIXTURE

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In a previous communication[1] it has been reported that freshly prepared alkaline Bordeaux mixture (5 : 5 : 50) consists of a gelatinous greenish-blue precipitate, which, in about 2 to 4 hours, changes to a deep blue solid. In the course of the present studies, it was observed that freshly prepared Bordeaux mixture contained a high initial concentration of copper in the aqueous phase (7 to 4 mg. cu. per l.) which decreased on standing to 0·50 mg. in 2 days. A further decrease to 0·47 mg. occurred, only very slowly. The results of a typical experiment are given in Table I. The general experimental procedure in this study was the same as has been described in the earlier paper.[1] Bordeaux mixture (5 : 5 : 50) was prepared by adding a 10% solution of copper sulphate to a well-stirred suspension of calcium hydroxide in a suitable amount of water. The precipitate was filtered at intervals, through a Jena sintered-glass filter I.G. 4, using the automatic filtering device. The aqueous phase was analysed for copper by the colorimetric method using sodium diethyl-dithio-carbamate and OH^-, CA^{++}; and SO_4^{--} were estimated by the usual analytical methods.

TABLE I

Ageing of Bordeaux Mixture at 24° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
1 hour ..	Greenish blue	4·21	0·0486	0·0195	0·0290
2 hours ..	do	2·69	0·0453	0·0196	0·0257
5 hours ..	Deep blue	0·59	0·0348	0·0195	0·0153
8 hours ..	do	0·56	0·0337	0·0195	0·0143
24 hours ..	do	0·53	0·0329	0·0197	0·0134
2 days ..	do	0·49	0·0326	0·0197	0·0128
5 days ..	do	0·48	0·0322	0·0197	0·0123
15 days ..	do	0·47	0·0321	0·0199	0·0123
1 month ..	do	0·47	0·0320	0·0199	0·0121
3 months ..	do	0·47	0·0324	0·0203	0·0122

From column 3, Table I, it will be noticed that there is a gradual decrease in the concentration of copper with time. The colour of the precipitate also

undergoes a change. The gelatinous greenish blue precipitate originally formed, changes to a compact deep blue solid after about 2 hours. This change in colour is accompanied by a fall in the concentration of copper in the aqueous phase.[1]

The ageing of precipitates is a well-known phenomenon and several crystalline precipitates have been found to undergo on ageing, a decrease in solubility. It was therefore considered to be likely that the fall in concentration of copper in the aqueous phase of Bordeaux mixture was due to ageing.

It will be seen from column 6, Table I, that the aqueous phase was initially supersaturated in regard to calcium sulphate. To eliminate any possible effect of this supersaturation on changes in copper concentration, the Bordeaux mixture was prepared under conditions wherein supersaturation with respect to calcium sulphate was obviated by taking appropriate quantities of water, copper sulphate and lime. To ensure however, that the aqueous phase was saturated in respect of calcium sulphate, a moderate excess of solid calcium sulphate dihydrate was added to the Bordeaux mixture, a few minutes after its formation, while the mixture was being vigorously stirred. Filtrates from this mixture were periodically collected and analysed. The results are given in Table II.

TABLE II

Ageing of unwashed Bordeaux mixture in water saturated with lime and calcium sulphate

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
2 hours ..	Greenish blue	0·93	0·0322	0·0200	0·0123
5 hours ..	Deep blue	0·57	0·0321	0·0198	0·0124
24 hours ..	do	0·53	0·0322	0·0199	0·0125
5 days ..	do	0·48	0·0321	0·0199	0·0124
1 month ..	do	0·47	0·0322	0·0199	0·0124

A small quantity of the precipitate from the above mixture was filtered at a Jena sintered glass filter and rapidly washed with an aqueous solution saturated with calcium sulphate as well as with calcium hydroxide. The

precipitate was then allowed to age in a solution of the same composition as employed for washing the precipitate of Bordeaux mixture. Filtrates from the above mixture were collected at different intervals and analysed. The results are given in Table III.

TABLE III

Ageing of washed Bordeaux mixture in presence of water saturated with lime and calcium sulphate

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
2 hours ..	Greenish blue	2·52	0·0335	0·0211	0·0124
5 hours ..	Deep blue	0·76	0·0328	0·0205	0·0123
24 hours ..	do	0·68	0·0326	0·0205	0·0123
5 days ..	do	0·63	0·0329	0·0204	0·0125
1 month ..	do	0·59	0·0328	0·0204	0·0124

A comparison of the data presented in Tables I, II and III shows that the initial supersaturation of the aqueous phase in regard to calcium sulphate, that normally occurs in the preparation of Bordeaux mixture, has little influence on the ageing of the Bordeaux mixture. The Bordeaux mixture that has been washed and then subjected to ageing in water saturated with calcium hydroxide and sulphate, seems to age a little more slowly as can be gathered from the copper values noted in column 3 of Tables II and III. From the above experiment, it may be concluded that the freshly formed precipitate has relatively a high solubility, due to the presence of fine primary particles. On standing, the fine particles undergo aggregation to larger units having a lower solubility.

A progressive decrease in the solubility of freshly prepared cupric hydroxide has been observed, on ageing, in several systems, as already reported in the earlier paper.[1] In all these cases, the variation of copper in solution, with time, is due to the phenomenon of ageing.

The rate of ageing of the precipitate in Bordeaux mixture is considerably influenced by temperature. This aspect was investigated by preparing samples of Bordeaux mixture at 0° C. and at 70±2° C. and studying the changes in the concentration of copper in these systems. The experimental results of the system at 0° C. are given in Table IV.

TABLE IV

Ageing of Bordeaux Mixture at 0° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
3 hours ..	Greenish blue	13·0	..	0·0232	0·0274
24 hours ..	do	10·8	0·0505	0·0242	0·0262
5 daya ..	do	7·7	0·0502	0·0246	0·0259
15 days ..	Deep blue	0·96	0·0477	0·0231	0·0245
2 months ..	do	0·72	0·0348	0·0242	0·0108

In this system, copper in solution is found to decrease very slowly (Column 3, Table IV) showing that ageing takes place more slowly at 0° C. The initial concentration of copper (13 mg. Cu/litre) is higher than in the mixture prepared at room temperature (24° C.) because in the case of the system at 0° C., measurement of solubility could be made before any appreciable aggregation of the precipitate had taken place. It is also very significant that the transformation of the gelatinous greenish blue precipitate to the deep solid occurred at 0° C., 10 days after the preparation of the sample, while the same transition occurred in 2 to 4 hours at 24° C.

To investigate the system at a higher temperature, Bordeaux mixture was prepared at 70° and was maintained at that temperature by immersing the bottle containing it, in a water thermostat. The bottle was provided with a water-cooled condenser and a soda lime tube and the mixture was filtered at suitable intervals and analysed. The results are given in Table V.

The greenish blue precipitate formed in this case turned deep blue within an hour of its formation. A small part of the precipitate turned black in three hours but the bulk of the precipitate remained deep blue. The continuance of the deep blue colour, in spite of the presence of the black particles of cupric oxide, is evidence of the stabilising influence of calcium sulphate on Bordeaux mixture. Copper hydroxide, it may be pointed out, is stabilised even at 100° C. by small amounts of manganese sulphate and other salts.[2,3]

A comparison of the data presented in Table V with those of Table I indicates that the initial concentration of copper at 70° C. is lower than that

TABLE V

Ageing of Bordeaux mixture at 70° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
1 hour ..	Deep blue	1·49	0·0257	0·0114	0·0143
5 hours ..	do	0·46	0·0251	0·0128	0·0123
24 hours ..	do	0·42	0·0253	0·0130	0·0123
5 days ..	do	0·36	0·0256	0·0132	0·0124

in Bordeaux mixture at 24° C. and falls off rapidly with time, due to the increased rate of ageing.

SUMMARY

Bordeaux mixture (5 : 5 : 50) prepared at room temperature (24° C.) contains a high initial concentration of copper in the aqueous phase (4 to 7 mg. copper/litre). On keeping the mixture at 24° C. the copper content of the solution decreases, and in a few days, attains a steady value of 0·47 mg. copper per litre.

The changes in copper concentration of the aqueous phase are due to the ageing of the precipitate. Experiments conducted at 0° and at 70° C. show that an increase in temperature markedly promotes ageing.

In the initial stages of formation of Bordeaux mixture, the aqueous phase is supersaturated with calcium sulphate, but the supersaturation does not influence in any way the ageing of the precipitated Bordeaux mixture. If, soon after its formation, the Bordeaux mixture is washed with water saturated with lime and with calcium sulphate, the rate of ageing of the solid is slightly reduced.

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ANALYSIS OF THE RAMAN SPECTRA OF POTASSIUM AND AMMONIUM ALUMS

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1. Introduction

Recently, Couture and Mathieu (1948) have shown that in the case of cubic crystals, the intensity and depolarisation of the Raman lines due to oscillations which are not totally symmetric vary with the directions of incidence and observation. This fact has been utilised to examine the experimental results in the case of a number of cubic crystals, *viz.*, K_2SnCl_6, $K_2Zn(CN)_4$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Pb(NO_3)_2$, $NaClO_3$ and $NaBrO_3$. Since potassium and ammonium alums also crystallise in the cubic system, their Raman spectra were investigated by the author with the help of the ultraviolet technique and analysed in the light of the detailed work by Mathieu and Couture (*loc. cit.*). But in the meantime a note has appeared on the Raman spectrum of the potassium alum (Mathieu and Tobailem, 1950). However, as the spectra recorded by the author seem to be more complete, it was felt desirable to place on record the results dealt with below.

2. Experimental Details

The crystals were grown from aqueous solutions by the method of slow evaporation. Clear transparent specimens, having cubic, octahedral and dodecahedral faces were chosen and were cut in the form of a rectangular parallelopiped having dimensions $1{\cdot}5 \times 1{\cdot}5 \times 1$ cm. To get a complete Raman spectrum, the crystal was mounted adjacent to the quartz arc specially designed to give very intense resonance radiation. Using a Hilger medium quartz spectrograph with a slit-width of 0·035 mm. exposures of the order of twenty-four hours were given to get fairly intense spectrograms. The polarisation pictures were obtained by using a Hilger Intermediate spectrograph with the optical arrangement described in an earlier communication (Padmanabhan, 1951). An arbitrary value of 20 is assigned to the intensity of strongest line in each spectrogram and visual estimates of the intensities of all other lines are expressed in relation to this figure.

3. Results and Discussion

Photographs of the Raman spectra of potassium and ammonium alums are reproduced in Figs. 1 and 2 respectively. The Raman spectra of the two alums exhibit twenty-one lines and two broad bands, the frequency shifts of which together with the relative intensities are tabulated in Table I. The frequencies observed by Matheiu and Tobailem are also entered in the same table. Most of the lines in the lattice region for the two alums have been recorded for the first time. The line at 621 reported by Mathieu and Tobailem could not be identified in the spectrum of potassium alum as it would fall adjacent to the mercury line λ 2576. It is indeed surprising to note that in the spectrum of ammonium alum no Raman lines due to the oscillations of the ammonium ion were recorded.

Table I

Author		Pot. alum M. and T.	Author		Pot. alum M. and T.
Pot. alum	Amm. alum		Pot. alum	Amm. alum	
52	56		528	528	527
64	68				621
85		87	986	986	977
105	103		995	994	995
115	112				
160	162		1107	1107	1107
170	172		1117	1120	
192	193				
		199	1131	1131	1131
203	207				
232	240				1214
320	318				
332	328	326			1384
443	448				
			3380	3357	3382
454	452	454			
			3528	3540	3525
465	465	465			

Potassium and ammonium alums crystallise in the cubic class with four molecules in a unit cell (space group T_h^6). Their crystal structures have been analysed by Lipson and Beevers (1935). Taking potassium alum, $KAl(SO_4)_2 12 H_2O$, as the typical example of the series, they found that the eight metal atoms take positions at the corners, centre, centre of faces and mid-points of the edges of the cell. The eight sulphur atoms in each cell must be distributed one in each small cell, on the trigonal axis. Eight of the oxygen atoms would be arranged similarly to the sulphur atoms, while the remaining twenty-four would be in general positions.

TABLE II

T_h	E	$8C_3$	$3C_2$	i	$3\sigma_h$	$8S_6$	n_i	T	T'	R	n_i'	R	I
A_g ..	1	1	1	1	1	1	5	0	1	1	3	a	f
A_u ..	1	1	1	−1	−1	−1	7	0	3	1	3	f	a
E_g* ..	2	−1	2	2	2	−1	5	0	1	1	3	a	f
E_u* ..	2	−1	2	−2	−2	1	7	0	3	1	3	f	a
F_g ..	3	0	−1	3	−1	0	15	0	3	3	9	a	f
F_u ..	3	0	−1	−3	1	0	21	1	8	3	9	f	a
$U_R(n_i)$ ..	48	5	0	8	0	5							
$U_R(S)$ ..	16	3	0	8	0	3							
$U_R(S-v)$	8	2	0	8	0	2							

(* = separately degenerate; a = active; f = forbidden)

The above character table is derived by taking aluminium, potassium and sulphate ions as separate groups and neglecting the molecules of water of crystallisation.

Of the twenty nine normal modes of external oscillations, 10 are permitted to appear in Raman effect and the rest in infra-red absorption. Of these ten Raman-active frequencies, two are symmetric, two are doubly degenerate and the rest are triply degenerate. It is satisfactory to note that the lattice spectrum of potassium alum exhibits ten frequency shifts (52 to 232 cm.$^{-1}$) in accordance with the analysis made above.

POTASSIUM ALUM

Polarisation results.—In the case of cubic crystals, there exist three types of oscillations A_g, E_g and F_g. The depolarisation factor of the lines belonging to these oscillations will be different for different orientations of the crystal. According to Couture and Mathieu (*loc. cit.*), there are seven possible crystal orientations for study. In the present investigation, only three cases are studied. They are (1) incident light perpendicular to cube face and scattered light perpendicular to dodecahedral face (case 2 *a* according to the notation used by Couture and Mathieu); (2) incident light perpendicular to dodecahedral face and scattered light perpendicular to cube face (case 2 *b*), and (3) incident light perpendicular to octahedral face and scattered light taken at right angles to it (case 3 *a*). The depolarisation factors

for oscillations falling under the different types for the three cases 2 *a*, 2 *b* and 3 *a* are given in Table III.

TABLE III

Type \ Case	2*a*	2*b*	3*a*
A_g ..	0	0	0
E_g ..	0	8	2
F_g ..	2	½	2/5

The values of the depolarisation factor estimated visually for the observed Raman lines are entered in Table IV. In Figs. 3 and 4 are reproduced spectrograms corresponding to the settings 2 *a* and 3 *a* in the case of potassium alum.

External Oscillations.—Out of the 10 lines allowed, 5 are of translatory and 5 are of rotatory type. Due to the presence of four molecules in the unit cell, the rotation of a sulphate ion round the three-fold axis gives rise to one A_g and one F_g. Since these movements involve very little change in polarisability the corresponding Raman lines may be expected to appear feebly in the spectrum. The two lines observed at 232 (A_g) and 203 (F_g) may be assigned to these two modes. The rotation of the SO_4 ion around an axis perpendicular to trigonal axis (which will be a doubly degenerate oscillation) by coupling splits into one E_g and two F_g, the corresponding lines of which will be intense. The two close lines 160 (F_g) 170 (F_g), and the line at 192 (E_g) may be assigned to these modes of oscillations.

The Raman active translatory types of oscillations arise only due to the movements of centre of gravity of the SO_4 ion, the metallic ions being stationary. The translatory movement of the SO_4 ion along the triad axis gives rise to one A_g and one F_g mode. The line 115 which exhibits polarisation values characteristic of F_g may be attributed to this mode of oscillation. Of the four other lattice lines, the only line of A_g type is the one at 52 cm.$^{-1}$ The assignment of this line to A_g mentioned above is questionable, since the two lines should be very near each other and not so far removed. The displacement of the SO_4 ion in a direction perpendicular to C_3 gives a group of 1 E_g and 2 F_g modes. Table IV shows that the lines 64 and 105 are F_g and E_g and hence they may be classified as belonging to this group. The line at 85 cm.$^{-1}$ is very feeble and hence its assignment to E_g type is doubtful.

TABLE IV

Line	Polarisation values			Type
	Case 2*a*	Case 2*b*	Case 3*a*	
52	0	·0	0	A_g
64	1·5	0·5	0·5	F_g
85	..	1·5	..	E_g
105	0	2·0	1·5	E_g
115	1·0	0·5	0·5	F_g
165	1·5	0·5	0·5	F_g
170	2·0	0·5	0·5	F_g
192	0·0	2·0	0·5	E_g
203	2·0	0·5	0·5	F_g
232	0	0	0·5	A_g
320	0	0	0	A_g
332	1·5	0·5	0·5	F_g
443	2·0	0·5	0·5	F_g
454	0	0·5	1·0	E_g
465	1·5	0·5	0·5	F_g
528	0·5	0·5	..	A_g+F_g
986	0	0	0	A_g
995	0	1·5	1·5	E_g
1107	0	2·0	0·5	A_g+F_g
1117	2·0	0·5	0·5	F_g
1131	2·9	0·5	0·5	F_g
3380	..	..	..	..
3528	..	..	..	..

Internal Oscillations.—Because of its tetrahedral symmetry the free sulphate ion has four distinct modes of oscillation of which ν_1 is single, ν_2 is doubly degenerate, and ν_3 and ν_4 are triply degenerate. The corresponding Raman shifts are 980, 458, 615 and 1105 cm.$^{-1}$ In a crystal, due to the presence of four molecules, the symmetric line gives rise to A_g and one F_g,

FIG. 2 FIG. 1

FIG. 1. Raman Spectrum of Potassium Alum

FIG. 2. Raman Spectrum of Ammonium Alum

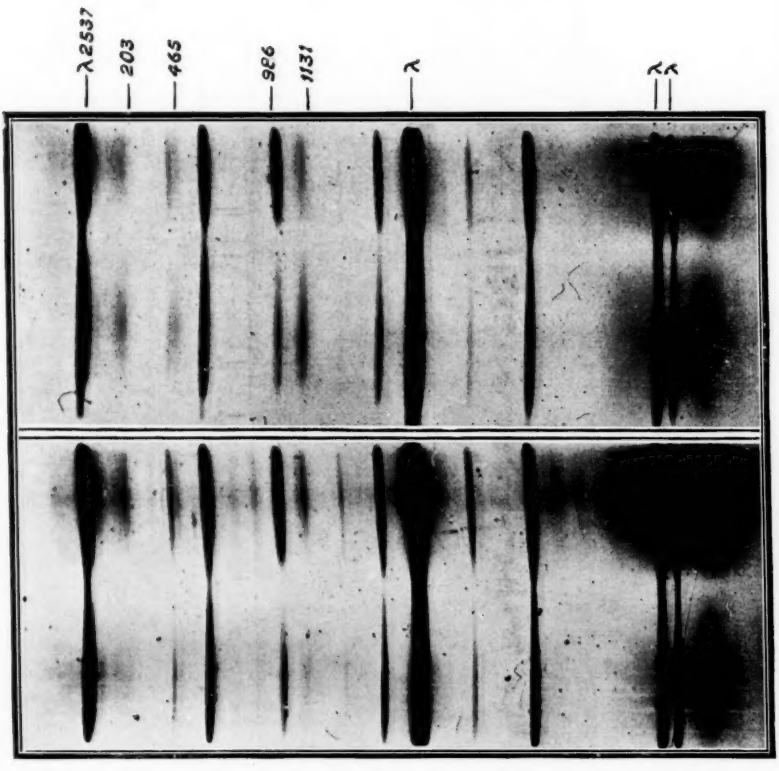

FIG. 3

FIG. 4

FIG 3. Raman Spectrum of Potassium Alum Case *2a*

FIG. 4. Raman Spectrum of Potassium Alum Case *3a*

the doubly degenerate line splits into E_g, $2F_g$ and the two triply degenerate lines give a group A_g, E_g, $3F_g$ separately. The total number of Raman-active lines should therefore be fifteen in accordance with the number of lines derived in the character table given above. Table V gives the lines due to the sulphate ion observed as well as the predicted lines in the case of potassium alum.

TABLE V

Free ion	A 980		E 458		F 615			F 1105		
In the crystal (predicted)	A_g	F_g	E_g	$2F_g$	A_g	E_g	$3F_g$	A_g	F_g	$3F_g$
Crystal (Author)	986 A_g	995 E_g	443 F_g	454 465 E_g F_g	528 A_g+F_g	–		1107 A_g+E_g	1117 F_g	1131 F_g
,, (M. & T.)	977 A_g	995 A_g+E_g	–	454 465 E_g F_g	527 E+F	621 E+F		1107 E_g	–	1131 F_g

The agreement between the predicted and observed lines are indeed satisfactory except for the discrepancy that the symmetric line splits into A_g and E_g, whereas it should have been A_g and F_g.

The lines at 320 and 332 cm.$^{-1}$—The two faint lines may be attributed to the symmetric oscillation of the octahedral group $Al(OH_2)_6$. According to X-ray analysis, the 12 water molecules are arranged in two sets, six of them forming an octahedral arrangement round the metallic ion. The symmetric oscillation of such a group should split into A and F due to coupling and it is actually found that the lines 320 and 332 exhibit polarisation values characteristic of A_g and F_g types.

The frequencies due to water molecules $\sim$3380 and 3528 cm.$^{-1}$ were found to be very broad and they could not be correctly classified.

The polarisation values of the lines of ammonium alum were found to be identical with that of potassium alum and so they are not given separately. The assignment of the lines both internal as well as external may be carried out similarly. The ammonia lines did not appear in the spectrum even after prolonged exposures.

My sincere thanks are due to Professor R. S. Krishnan for the stimulating suggestions and encouragement.

4. SUMMARY

The paper reports the results of a detailed study of the Raman spectra of single crystals of potassium and ammonium alums using λ 2536 radia-

tion as exciter. The recorded spectrum of each crystal exhibits 10 lattice lines and 13 internal lines. A study has also been made of the effect of crystal orientation on the polarisation of the Raman lines. From the observed variations in intensity and polarisation, proper assignments have been given both to the external and internal lines.

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